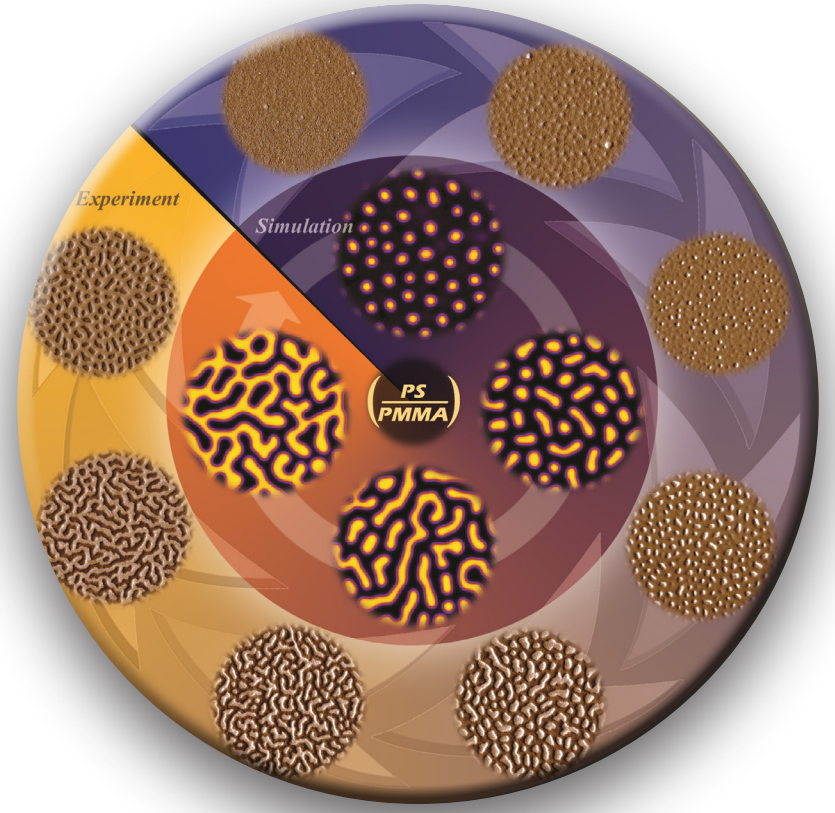
# CINT

## The Center for Integrated Nanotechnologies




# 2012 Annual Report

# Center for Integrated Nanotechnologies
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Cover art - Mapping the Phase Behavior of Polystyrene (PS)/Poly(methyl methacrylate) (PMMA) Brushes. Image credit: Dale Huber

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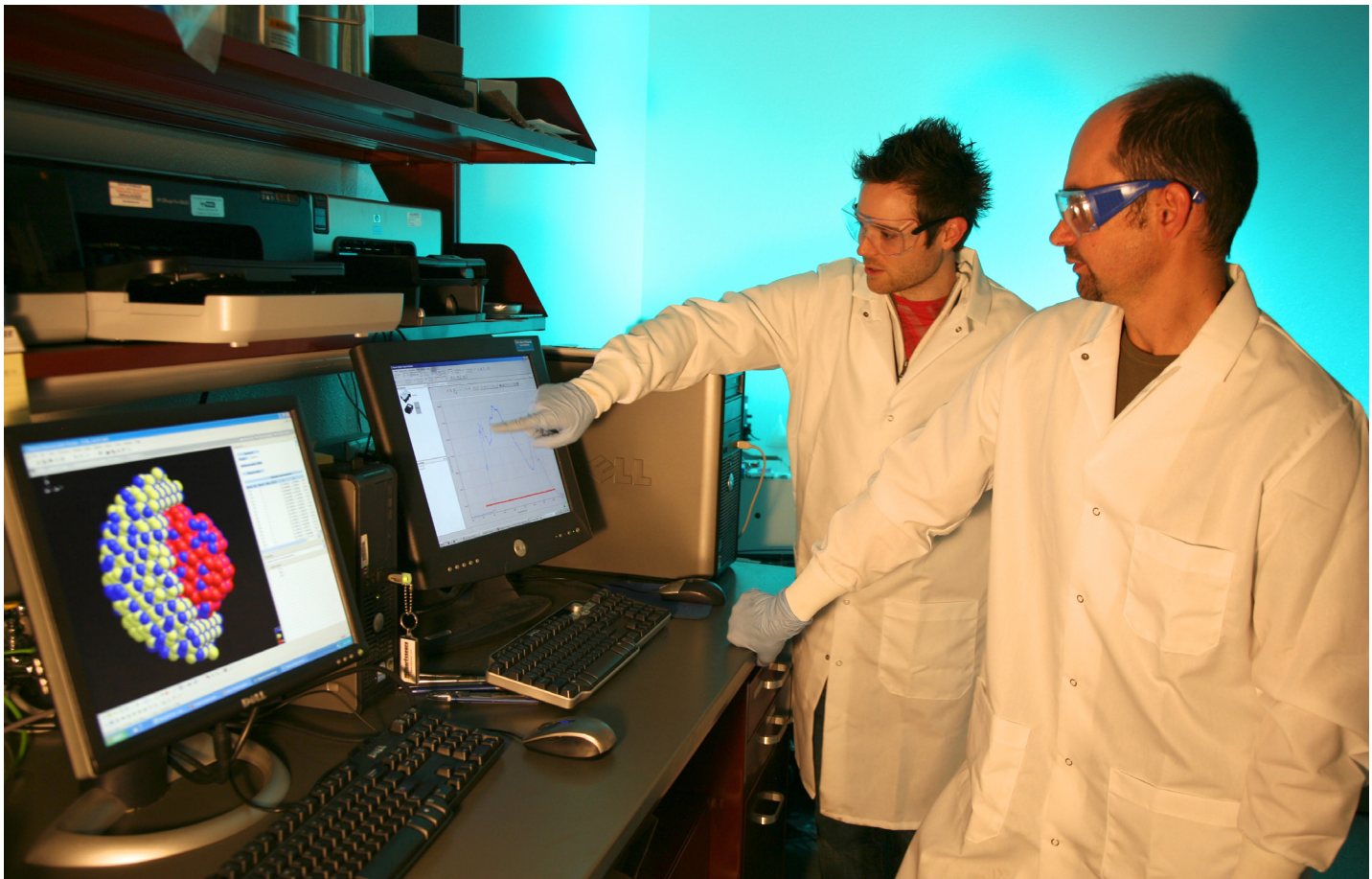


# From the Director's Office

Thank you for your interest in the Center for Integrated Nanotechnologies (CINT). We are pleased to present the *CINT 2012 Annual Report*. With more than 350 visiting researchers ("users") utilizing our two Facilities throughout the year and over 200 scientific papers published, no single document could accurately represent the breadth and impact of the research performed by the CINT scientific community. Instead, we hope that the technical highlights and program information herein will inspire you to learn more about CINT and subsequently join our growing community of users at the exciting scientific frontier of nanoscience integration.

As a Department of Energy/Office of Science national user facility, CINT plays a leadership role in building a scientific community focused on the creation, characterization, understanding and *integration* of nanostructured materials. Through technical events such as the CINT User Conference (September 18-20) and the jointly-organized Workshop on Nanoparticle Science (November 5-6), we engage with others to identify research opportunities and define the future capability needs. Our outreach efforts have expanded and include a variety of communication modes targeted to specific audiences.

In response to our semi-annual and rapid access user proposal calls, user demand continues to exceed availability and quality remains high; approximately one third of all CINT publications appear in high-impact journals. Also notable is that half of all user proposals request two, three or more CINT scientists and their associated capabilities. Clearly the ability to form a collaborative team is valued by our users and an important role of a nanoscience user facility. In fact, CINT *Integration Focus Activities* (page 11) are explicitly designed to encourage such interdisciplinary collaboration by users and staff on topics that involve specific integration challenges, materials systems or use-inspired basic research.

Our scientific, administrative, and technical staff are the real source of our ongoing success. Again this year, we feature two CINT scientists in this Report and encourage you to learn more about them and their colleagues via the "people" page on our website. The retirement and career advancements of several CINT scientists this year created opportunities for us to hire impressive new staff members to launch new research areas and expand our capability base. We continue to design, refine and develop our signature *Discovery Platforms*™ (page 8), which are micro-fabricated structures and devices that enable nanoscale experiments never before possible.

We will especially miss Tom Picraux who retired after many decades of exceptional scientific and management leadership at both Los Alamos and Sandia National Laboratories. As CINT Chief Scientist, Tom was instrumental in launching CINT and establishing a seamless CINT partnership for the future.

As the United States enters the second decade of the National Nanotechnology Initiative, we are reminded that the enduring public interest in nanotechnology reflects the expectation that scientific understanding is the pathway to unprecedented benefits for humankind. We are committed to fulfilling that expectation.

David Morris, Director

Neal Shinn, Co-Director

Tom Picraux, Chief Scientist

Heather Brown,
User Program Manager

Antonya Sanders,
Comm & Outreach Manager

# About CINT

Nanotechnology is the creation and use of materials, devices and systems through the control of matter at the nanometer-length scale, and at the level of atoms, molecules, and supramolecular structure. Nanoscience will explore and develop the rules and tools needed to fully exploit the benefits of nanotechnology. It will fundamentally change the way materials and devices will be produced in the future and subsequently revolutionize the production of virtually every human-made object.

The Center for Integrated Nanotechnologies (CINT) is a Department of Energy/Office of Science Nanoscale Science Research Center (NSRC) operating as a national user facility devoted to establishing the scientific principles that govern the design, performance, and integration of nanoscale materials. Jointly operated by Los Alamos and Sandia National Laboratories, CINT explores the continuum from scientific discovery to use-inspired research, with a focus on the integration of nanoscale materials and structures to achieve new properties and performance and their incorporation into the micro- and macro worlds. Through its Core Facility at Sandia National Laboratories and its Gateway Facility at Los Alamos National Laboratory, CINT provides open access to tools and expertise needed to explore the continuum from scientific discovery to the integration of nanostructures into the micro- and macro worlds. In its overall operations, CINT strives to achieve the following goals common to all Nanoscale Science Research Centers:

1. Conduct forefront research in nanoscale science;
2. Operate as a user facility for scientific research;
3. Provide user access to the relevant BES-supported expertise and capabilities at the host national laboratory;
4. Leverage other relevant national laboratory capabilities to enhance scientific opportunities for the nanoscience user community;

These additional goals are specific to the unique CINT mission:

1. Establish and lead a scientific community dedicated to solving nanoscale science integration challenges;
2. Create a single user facility program that combines expertise and facilities at both Los Alamos and Sandia National Laboratories.

The CINT user program provides the international scientific community with open access to world-class scientific staff and state-of-the-art facilities for theory and simulation, nanomaterials synthesis and characterization, and unique capabilities for nanoscale materials integration, from the level of nanoscale synthesis to the fabrication of micro- and macroscale structures and devices. The staff of CINT includes laboratory scientists, postdocs and technical support staff who are leaders in the nanoscience research programs in CINT scientific thrust areas:

Nanoscale Electronics and Mechanics,
Nanophotonics and Optical Nanomaterials,
Soft, Biological and Composite Nanomaterials, and
Theory and Simulation of Nanoscale Phenomena.

The thrusts have been developed over the past several years by engaging the broader scientific community through discussions with potential CINT users and with attendees at CINT workshops, as well as by attracting some of today's top nanoscience talent to become CINT staff.

# New Capabilities

Time-Resolved Photoluminescence:

Photoluminescence (PL) and its temporal dynamics constitute one of the most fundamental techniques for uncovering fundamental physical properties of nanomaterials and their coupling to the environment. A comprehensive time-resolved photoluminescence (TRPL) system was acquired that covers a very wide spectral range (~350nm–1600nm), a large span of timescales (150 femtoseconds(fs)– milliseconds), variable excitation wavelengths (ultraviolet(UV) to 1050nm) and temperature ranges from 3K to above room temperature. Such a complete time-resolved PL system provides a centralized facility at CINT and other NSRCs for time-resolved measurements of single nanoparticles and their ensembles. The uniqueness of this system is primarily in the multiple detection modalities (upconversion, photon counting and streak camera) and high stability provided by a state of the art Ti-sapphire laser oscillator (>3.5W average power) in conjunction with doubler and tripler attachments.

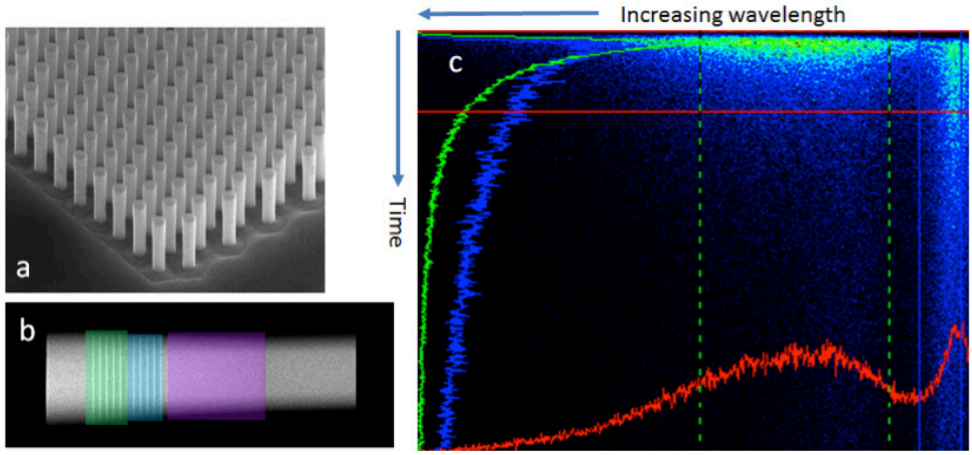



Figure 1: Emission lifetime measurement of two color InGaN quantum wells heterostructure using streak camera. (a) SEM picture of photonic crystal laser composed of nanowire array. (b) Representation of a TEM image of a single nanowire removed from the photonic crystal sample. (c) Emission lifetimes of blue (430nm) and green (520nm) InGaN quantum wells from the planar (pre-etched) material. Traces on the left are temporal profiles of spectrally integrated emission of blue and green quantum wells. The red trace is time integrated emission spectrum. These measurements illustrate that the blue quantum well is of much higher quality and therefore has a narrower spectra and a longer lifetime. The green quantum well shows large broadening and a short lifetime.

The system has been in operation for less than a year and we have already several projects using this system. One the projects is to investigate the exciton dynamics and energy transfer in hetero-layered structures of single-layer metal chalcogenides, such as $MoS_2$, $MoSe_2$, $WSe_2$ and others. The samples are prepared with controlled number of BN spacers between the layers, which allows for the controlled coupling between the layers. A high-efficiency microscope built specifically for the TRPL system provides diffraction-limited lateral resolution allowing the study of spatial dynamics on micron-size exfoliated samples. Another project using this system aims at the study of quantum dot-quantum dot interactions through emission lifetime measurements. The strength of the interaction is controlled by the distance between quantum dots changed by hydrostatic pressure created inside a diamond anvil device.

One last example of a user project using this capability is the study of the correlation between material quality, emission lifetimes and their spectral profiles. Figure 1 shows the dramatic difference between the blue and green emitting InGaN quantum wells that are used in the active medium of a nanowire photonic crystal laser. These results show that the high quality material (blue emission) has a longer lifetime and narrower linewidth due to smaller non-radiative recombination rates, whereas the poorer quality green quantum wells have shorter lifetimes and broader emission spectra. Contact: Igal Brener.

Holographic optical trapping and force measurement system:

One of the greatest challenges in developing miniaturized and functional integrated systems from complex nanoscale components, particularly soft components, is the difficulty involved in non-destructively manipulating delicate materials and solvent stabilized nanostructures. It is highly desirable to be able to catch, move, and release materials and their aggregates in a controlled manner without damaging or dramatically changing the chemical and physical properties of these structures. The controlled integration of nanostructures into soft matrices to create hybrid composite materials is of particular importance. In meeting nanoscience integration challenges, there is also a great need to understand mechanical interactions at soft interfaces, from single intra-and intermolecular interactions to the response between microscopic cells and nanostructured surfaces across multiple length-scales.

We are addressing these challenges in nanosystems integration and force characterization by bringing to CINT a new capability for the non-contact optical manipulation of delicate soft materials and particles that can also mechanically probe interactions of such materials in situ. The instrument is comprised of a modular optical trapping fluorescence microscope that enables the non-contact 3-dimensional manipulation of trapped objects and a force measurement module capable of measuring interaction forces on the order of 0.1-900 pN, allowing one to observe the unfolding of supramolecular structures, the action of molecular motors, and measure the surface adhesion forces of biological cells. This laser trapping system complements the suite of top down and bottom up fabrication and manipulation methods at CINT, and fills a gap in the mechanical characterization in fluidic environments of soft structures composed of nanocomponents, such as biological and biomimetic materials and nanoparticles. We expect that the versatility of the system will be of great benefit to members of our user community interested in addressing the challenges of manipulating and interrogating the interaction between hard and soft nanomaterials in their native environments and integrating these components into composite nanomaterials and functional devices. Contact: Wally Paxton.

Furnace-Type Solid-Source CVD System for Nanowire Growth

A new furnace-type solid-source CVD system for nanowire growth has been operational since the middle of February 2012. This new CVD system is used for the synthesis of new materials including group III-V nanowires and their heterostructures, functional nanowires for thermoelectric applications, and topological insulators. The growth of InAs nanowires has been demonstrated. Moreover, the new CVD system will allow the growth of 2D-1D hybrid structures such as semiconductor nanowires on 2D structures like single-layered materials. This expanded materials synthesis capability will be integrated into other major areas of study at CINT. Contact: Jinkyoung Yoo.

Spatio-temporal imaging on the nanoscale.

The development of methods for tracking 3D molecular motion is an enabling technology spanning many fields, from fundamental cellular biology (e.g., biomolecular trafficking) to probing the dynamic organization of soft nanomaterials. Previously, the Werner and Goodwin laboratories within the SBCN thrust developed a fluorescence microscope capable of following motion of individual fluorescent NPs (e.g., Qdots) as they diffuse in 3D at rates comparable to protein trafficking in cells (i.e., μm/s). The approach employs a custom-built confocal microscope that uses a unique spatial filter geometry and active feedback 200 times per second. This unique CINT capability was applied by users B. Wilson (UNM) and D. Lidke (UNM) to study the 3D spatiotemporal dynamics of Qdot labeled individual proteins responsible for the human allergic response (Figure 2A). The work measured single protein interactions and dynamics throughout the 3D volume of a living cell. By 3D tracking of individual allergy receptors (IgE-FceR1), complex 3D topologies of the outer plasma membrane were mapped, including 3D nano-topologies that would be invisible by ordinary light microscopy (Figure 2B). The down-regulation and dynamics of the receptor being endocytosed was captured and the internal transport kinetics of the process was determined to be ca. 950 nm /s. The work suggests that receptors become transiently trapped during diffusion, thereby eliciting the allergic response. The imaging techniques developed by CINT scientists and applied to complex biological materials has provided molecular details of the human allergic response. Contacts: Jim Werner and Peter Goodwin.

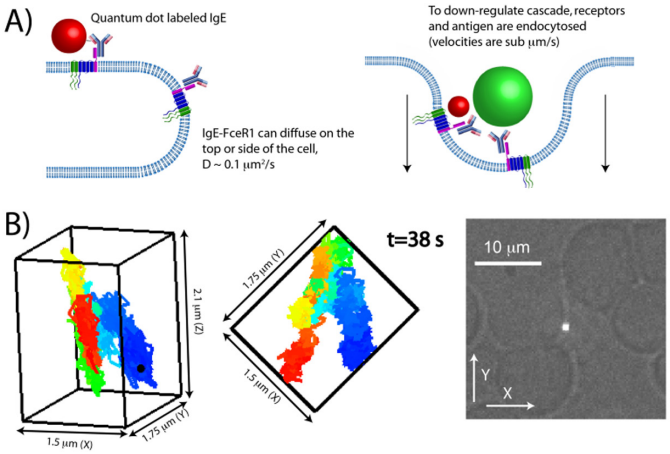



Figure 2 (A). Schematic of the IgE-FceRI system. The receptor can diffuse on the top or side of a mast cell. Following stimulation with a polyvalent antigen a signal transduction cascade is initiated, with down-regulation causing receptor endocytosis. (B). Two different views of a 3D trajectory of a single IgE-FceRI on the side of a rat mast cell. This trajectory traces out a 3D cell surface nanoscale topology that would not be visible by conventional imaging approaches (e.g. white light image on right hand side).

High Power THz system (Chen):

We will continue our effort in building a high power THz system based on tilted pulse front optical rectification method. It employs a Ti:sapphire amplifier with 100 fs pulse duration, 3 mJ/pulse energy, and 1 kHz repetition rate, to excite a $LiNbO_3$ crystal and generate intense broadband terahertz pulse with field strength >100 kV/cm (under diffraction limited focusing) and 1.5 THz bandwidth. Liquid helium cryostat will be integrated. This capability will enable a host of nonlinear experiments spanning metamaterials, semiconducting nanomaterials, and complex metal oxides. It will attract addition user projects where such a table-top high power THz system is essential. Contact: HouTong Chen.

FTIR Microscope

A Fourier-Transform InfraRed microscope system is capable of measuring infrared transmission and reflection spectra of samples with 10-micrometer resolution, which is near diffraction-limited for the wavelengths used. The system also possesses a spatial mapping capability allowing to build full IR hyperspectral image of the sample. Timeresolved measurements are possible with a step-scan capability included with the system. In the near future, ultrashort-pulse laser will be coupled to the microscope allowing localized sample excitation. Future plans also include coupling ultrashortpulse mid-IR supercontinuum pulses into the system for the purpose of full pump-probe interferometric capability in an all-reflective microscopy setup. Contact: Anatoly Efimov.

NanoSight LM10HSB Nanoparticle Characterization System

Coupled with image analysis software (Nanoparticle Tracking Analysis, NTA), this system allows automatic tracking and sizing of nanoparticles on an individual basis. Results are displayed as a frequency size distribution graph and output to spreadsheet. We aim to use the instrument to assess nanoparticle concentrations and bright/dark fractions, for example. Contacts: Jennifer Hollingsworth and Anatoly Efimov.

# Discovery Platforms

The thrusts develop a variety of new instrumentation to advance the science in their areas. One effort unique to CINT is the Discovery Platform™. These platforms are modular micro-laboratories designed and batch fabricated by CINT to allow easy integration of nanomaterials into microscale structures. Their purpose is to facilitate studies of nanomaterial properties and their integration. They should allow easy connections, a range of diagnostic and experimental measurement conditions, and a degree of standardization and reproducibility in nanoscale measurements. The inception, creation and evolution of Discovery Platforms have evolved in close collaboration with our user community. Most recently we have recognized the potential broad user community appeal to other experimental platforms that facilitate the synthesis of as well as work with nanoscale materials. In this spirit we have also recently introduced a Microfluidic Synthesis Discover Platform.

## Nanomechanics and Thermal Transport Discovery Platform (NMTTDP)

The purpose of the CINT Nanomechanics and Thermal Transport Discovery Platform (NTTDP) is to enable researchers to perform experiments related to nanomechanics, sensing, scanning probe microscopy, in-situ TEM, and magnetization measurements, all using structures on a single, small chip-based platform. A new version of this Platform also includes structures for measurements of the electrical properties, thermal properties, electromechanical behavior, and microcalorimetry of nanoscale samples (Figure 3).

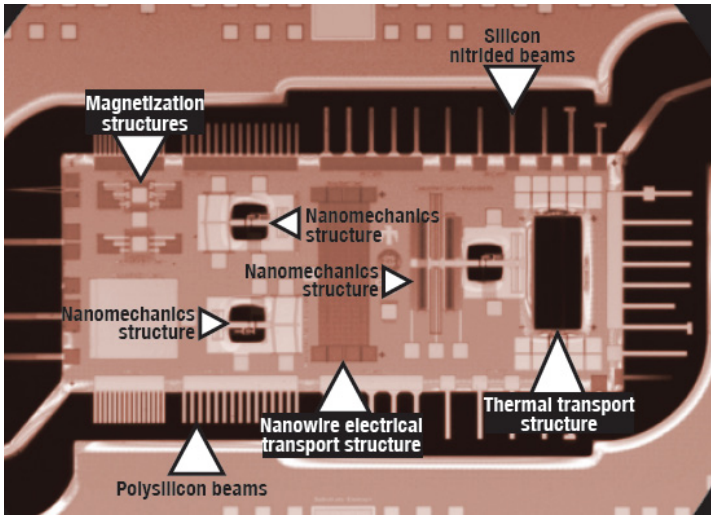



Figure 3: The NMTTDP contains test structure for the measurement of the mechanical, thermal, and electrical properties of nanoscale materials.

Both versions of this platform incorporate more than one hundred mechanical structures with sizes and spacings as small as 1 mm. These are located on a chip with dimensions of 1.5 mm by 3.5 mm by 0.6 mm – a size that is designed to fit most atomic force microscopes (AFMs) and many transmission electron microscopes (TEMs). The mechanical structures on the Platform can be used as sensors for force, displacement, and mass, and they may be functionalized easily for use as chemical sensors. Other parts of the micro-chip include electrostatically-driven and thermally-driven actuators that are able to provide tensile and compressive forces to nanoscale samples over a force range from less than $1 \times 10^{-6}$ N up to approximately $1 \times 10^{-4}$ N. In addition, holes have been etched through the chip to permit sample actuation with simultaneous *in-situ* TEM characterization.

This Discovery Platform has been heavily used by researchers for the study of the nanomechanics of semiconducting and metallic nanowires. In work performed by CINT user Prof. Dan Gianola and his research group at U. Penn, the NMTTDP was used to measure the piezoresistance of (100)-oriented silicon nanowires as a function of wire diameter and length. These studies required electrical testing during straining, which is one key feature that was added in the second generation of this nanomechanics test platform. Their studies revealed gauge factors comparable to values reported for thin film silicon and in contrast to the giant piezoresistance previously reported for silicon nanowires. In other work from the Gianola group, the NMTTDP was used to measure the temperature dependence of the onset of plasticity and fracture in FCC metal nanowhiskers [Figure 4(a)]. Gianola's group observed that the temperature and strain rate dependence to plasticity onset in Pd nanowhiskers did not follow conventional beliefs of thermally-activated dislocation nucleation, suggesting that plasticity onset in metal nanowhiskers is more complex than previously envisioned. This work was featured in nanomechanics symposia at the MRS and SES meetings with manuscripts in preparation. The NMTTDP was also used to study stress generation mechanisms in Li-ion battery anode electrode materials. In work that was performed in collaboration with CINT user Prof. Gerald Gulley of Dominican Univ., arrays of cantilever beams were coated with copper followed by a thin layer of silicon. The silicon-coated beams were cycled in battery electrolyte against a Li metal counter electrode, and the beam deflection was recorded as a function of cell potential [Figure 4(b)]. The cantilever deflection was recorded over several charge-discharge cycles in order to observe mechanical degradation in the silicon electrodes. The sensitivity of the cantilever beams to surface stress was found to be higher than the optical system could follow, which has led to a modified focus on processes that occur just at the electrode-electrolyte interface, e.g. the formation of the solid-electrolyte-interphase (SEI).

In the coming years we will continue to use this platform for the nanomechanical testing of metallic and semiconducting nanowires, with a special focus on understanding plastic deformation mechanisms in monocrystalline FCC metal nanowhiskers and mono and polycrystalline BCC metal nanowires. Nanomechanical testing of semiconducting nanowires will focus on measurement of the electromechanical response of NWs, i.e. the effect of strain on electrical conductivity. We will also continue to use the cantilever beam arrays on the NMTTDP to measure surface stress in Li-ion battery electrode materials during electrochemical cycling with a special focus on understanding the formation and evolution of the solid-electrolyte-

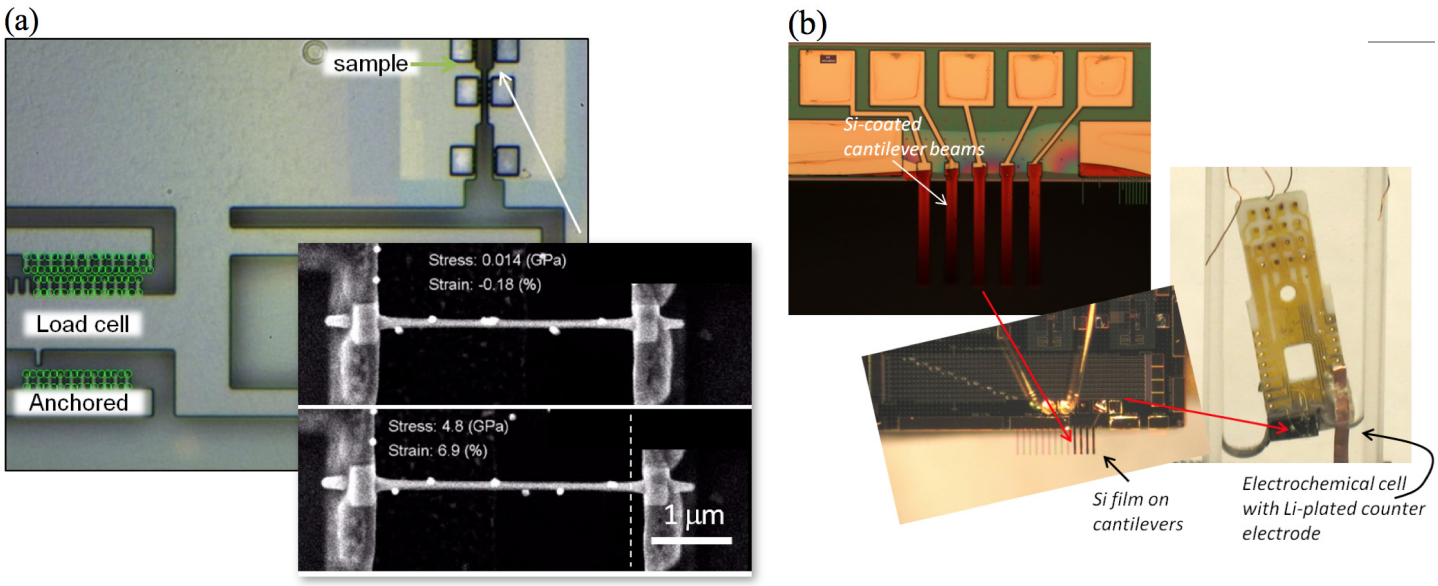



Figure 4.(a) Nanomechanical testing using the tensile test stage of the NMTTDP. A Pd nanowhisker is stressed to the point of fracture. The top inset image is the Pd nanowhisker in the unstressed state. The bottom inset image is the Pd nanowhisker with 4.8 GPa stress (6.9% strain) just prior to fracture. [From Prof. Gianola's group, U. Penn]. (b) Si-coated cantilever arrays on the NMTTDP used for measurement of stress generation during cycling in a Li-ion battery half cell. The image on the right shows the NMTTDP mounted on a chip carrier and immersed in battery electrolyte in a sealed cuvette for testing

interphase layer on silicon and on probing the chemical modification of passivating surface coatings applied to battery electrodes, such as ultra-thin aluminum oxide layers deposited by atomic layer deposition. In addition to nanomechanics measurements, the NMTTDP will be used to investigate the effect of strain on the optical and electronic structure of nanowires and two-dimensional semiconductors, such as bilayer graphene. We will use the thermal analysis test structures on the NMTTDP to determine the thermal conductivity in semiconductor alloy and core-shell nanowires using a pulsed heating method. The goal of these studies is to understand the influence of alloying, nanostructuring, and doping on thermoelectric efficiency.

## TEM Liquid Cell Discovery Platform

We have completed the successful fabrication and demonstration of a new CINT Discovery Platform that provides a unique capability to perform experiments inside a transmission electron microscope using volatile liquids, such as aqueous solutions or battery electrolytes. The TEM Liquid Cell Discovery Platform uses two microfabricated chips, each having a thin silicon nitride window (~ 40 nm thick), that permits transmission of high energy electrons with little attenuation. The two chips are mated face-to-face to create a narrow a cavity, approximated 100 nm thick, Figure 5. Liquids are inserted in this cavity through two fill holes, which are subsequently capped with epoxy to create a sealed liquid-filled chamber. Metal electrodes are also provided into the viewing region of the platform in order to permit the observation of electrochemical processes while imaging in the TEM. The platform has been tested with the assembly of $LiFePO_4$ Li-ion battery cathode nanoparticles, using dielectrophoresis, and with filling and imaging through an ethylene carbonate based Li-ion battery electrolyte. Future work with this platform will focus on imaging the formation and evolution of the solid-electrolyte-interphase layer on Li-ion battery electrodes.

We will use the newly fabricated TEM Liquid Cell DP to investigate electrochemical mechanisms at solid electrode – liquid elec-

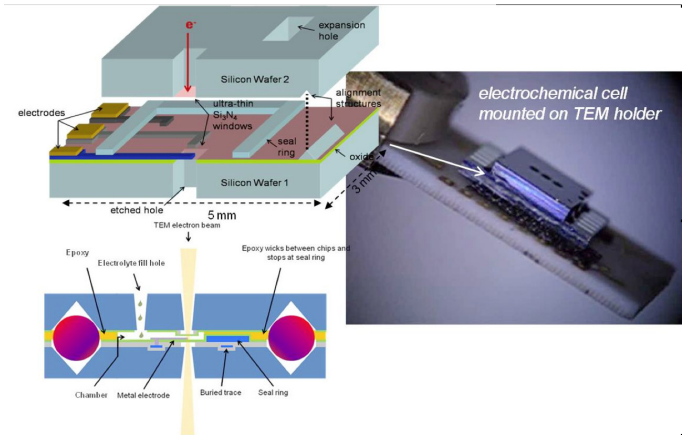



Figure 5. The TEM Liquid Cell Discovery Platform. Two microfabricated chips with electron transparent windows are mated face-to-face to create a thin cavity that is then filled with liquid and sealed. The image on the right shows the assembled platform on a TEM holder.

trolyte interfaces. This work is complementary to the in situ TEM work involving open electrochemical cells using ionic liquid or solid electrolytes, as described in the NEM thrust activities. The goal of these studies is to image the formation and evolution of the solid-electrolyte-interphase layer on representative Li-ion battery nanoscale electrodes, including silicon and graphite anodes and $LiFePO_4$ and $LiMnxO_2$ cathodes, while these electrodes are immersed in ethylene carbonate-based Li-ion battery electrolytes. The sealed cell geometry of the TEM Liquid Cell permits future experiments that are aimed at understanding cell aging mechanisms. These studies will be performed by cycling sealed cells outside the TEM for periods ranging from days to weeks interspersed with periodic TEM imaging and analysis. This offers a view into long time scale degradation phenomena, an approach normally not possible in TEM electrochemical experiments. As an exploratory activity, we will also test imaging of the TEM Liquid Cell Discovery Platform using aqueous solvents, with the goal of assessing the suitable of this platform for analysis of chemical synthesis or biology processes.

## Microfluidic Synthesis Discovery Platform


Figure 6. On chip synthesis of Au NRs. The reaction progresses throughout the serpentine channel as evidenced by the color change from pink to purple.

CINT has begun development of a new Microfluidic Synthesis Platform to advance both the science and practice of nanomaterials synthesis. The microfluidic system features an all-glass chip possessing a serpentine channel that can hold volumes from 200 μL to 1 mL (Figure 6). The microfluidic platform will permit rapid phase mapping of nanoparticle synthesis. The chip is positioned on a custom-made Al base plate that allows for precision temperature control between sub-ambient to 350°C. Real time reaction monitoring will be achieved through microscopy (visible and fluorescence) and UV-Vis spectroscopy. The chip is designed to include maximum flexibility for adjustment of reaction parameters, including temperature, time, control over reactant stoichiometry with real-time analysis of the particle properties and an automated fraction collector. The careful mapping of reaction conditions and kinetics will advance our understanding of the interplay between reaction conditions and particle morphology, improve reproducibility of nanoparticle synthesis, and lay the groundwork for scale-up / large-scale production of nanoparticles. Preliminary studies will center on the study of Au nanorod growth with dimensions of the rod determined in real time by optical spectroscopy. Introduction of this capability has already attracted interest from industry (Cabot Electronics). Introduction and further optimization of the discovery platform in concert with our user community will allow for fabrication of a microfluidic platform(s) that will enable the reproducible synthesis of nanoparticles.

# Integration Focus Activities

The IFAs emerge out of a particular thrust effort and build on areas of strength across our scientific thrusts. The studies center on particular classes of materials, systems, or phenomena and derive their integration focus through a use-inspired science approach. These focused efforts bring an interdisciplinary approach by CINT scientists and users to a particularly timely area of integration science. They enable rapid progress in specific areas of common interest, attract and build user communities, and are variable term in nature.

## Programmable Membrane-Based Nanocomposites

The focus of the Programmable Membrane-Based Nanocomposites (PMBN) Focus Area is to investigate the interactions between nanoscale materials and membrane-based composites such as lipid and polymer vesicles and membrane architectures. The ultimate goals of the research involve learning how to replicate many of the complex behaviors associated with cellular membranes within artificial nanocomposites and integrated systems. These integrated nanomaterials could be utilized in applications including electrical energy storage (the artificial electric eel), artificial photosynthesis, environmental remediation (reversible $CO_2$ sequestration and water purification), and responsive sensors and adaptive materials for Homeland Defense applications.

The starting point for understanding the behavior of complex membranes involves understanding the fundamental interactions between membrane hosts, nanoparticles, and substrate surfaces. Initially, research in this IFA focused on investigating interactions of nanoparticles with lipid-based membrane systems, including:

1. nanoparticle adsorption, insertion, migration, and aggregation as a function of particle size, shape, and surface chemistry,
2. lipid responses as mediated by substrate interactions, including diffusion and transport, mechanical stability, domain formation and component partitioning, and
3. membrane-mediated nanoparticle organization.

One highlight is on nanolithography using phase separating polymer brushes. Diblock copolymers and their phase separation are well established and have been extensively studied for decades. One area of significant interest and opportunity is the use of diblock copolymers for nanolithography, the process of directing diblock phase separation into well-ordered, device compatible structures. Progress in this area has been limited due to several noted drawbacks of diblock copolymers, including the need to spin coat onto planar substrates followed by slow annealing protocols to induce ordering. CINT Scientists Dale Huber and Amalie Frischknect, along with Glenn Fredirckson (UCSB) have examined both experimentally and computationally phase-separation in mixed homopolymer monolayers. Collectively, these studies showed that when compositionally different polymers are anchored to a common surface, phase separation occurs that is conceptually similar to the familiar behavior of diblock copolymers. Recent work has focused on developing a molecular-level understanding of the phase separation of poly(methyl methacrylate)-b-polystyrene (PMMA-PS). Self-consistent field theory (SCFT) was used to predict a phase diagram of the PMMA-PS system. Experimental determination of the phase behavior was conducted and revealed significant differences in the details of the predicted structures. Specifically, significantly shorter range ordering was observed experimentally. The reduced structural ordering could be replicated computationally by adding random variation in the monolayer graft density. The simulated grafting fluctuations served to mimic the radical initiation of a polymer chain on a surface as a stochastic process. A comparison between computationally predicted and experimentally determined structure is qualitatively shown in Figure 7. A number of possible approaches to improve the grafting density variations are currently under investigations. For example, Y-shaped initiators where each branch initiates a different polymer chain block (i.e. PMMA or PS) with high efficiency would serve to enforce regularity in grafting. While this is conceptually simple, synthetically it will represent a challenge. Alternatively, a spacer positioned below the initiator may allow for mobility to the graft point of each polymer. This approach would permit the graft points of the various polymer chains to rearrange slightly and function to even out variations in graft density. We anticipate that tightly coupled simulation and experiment will allow us to develop systems with long-range order in the next few years. We have also developed techniques to pattern the mixed brushes into micron scale features, which can phase separate into nanoscopic features. For example, once long range ordering has been achieved, a one micron line could be made to phase separate into one hundred 10 nm lines. This will open the door to simple and robust nanolithography methods that don't require planar substrates or lengthy and complicated processing.

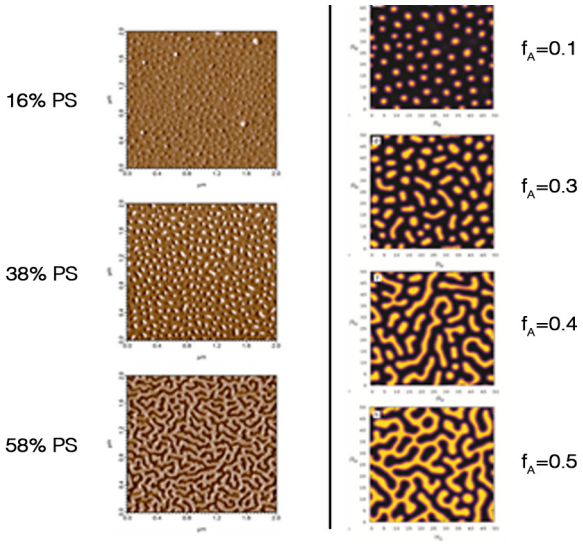



Figure 7. (A) AFM images of block copolymer phases. (B) Simulated block copolymer phase segregation

## Nanowires for New Energy Concepts

The novel properties of nanowires offer tremendous opportunities for transformative energy applications. These multi-purpose materials combine nanoscale and even quantum-confinement effects that enhance transport properties. CINT scientists together with our user community are focusing to understand and control the functionality and integration of heterogeneous semiconducting nanowires for new energy harvesting and storage concepts. We emphasize heterogeneous nanowires to realize an unprecedented level of control over material performance by tuning interface, strain, and materials-mixing effects. We combine new synthesis strategies with structural, electrical, optical, and thermal characterization, initially at the single-nanowire level to answer critical science questions underlying new nanowire materials concepts for photovoltaics, thermoelectrics, and energy storage. We also drive toward functional integration of nanowires into 2 and 3D architectures.

Recent theoretical contributions to this IFA include the following. CINT Scientist N. Modine and CINT User M. Stopa have developed tools for computing the electronic structure of semiconductor nanowire heterostructures, including the effects of multiple bands and position dependent strain. The Single Electron Tunneling Elements (SETE) code developed by Stopa has been modified to calculate the electronic structure of nanowires within a strain-aware version of the k dot p approximation. The local strain tensor within the nanowire is extracted from the atomic positions obtained by relaxing the structure using a classical Modified Embedded Atom Method potential. Working with CINT users H. Fehske and A. Alvermann, we have studied the effects of interactions with phonons on the behavior of electrons, holes, and excitons in nanowires. A new algorithm was developed to treat even very slow (adiabatic) phonons in a fully quantum, numerically exact way. The quasiparticle mass and other properties were calculated. With CINT user J. Bonca, we have modeled the fully quantum dynamics of a coupled electron-phonon system (polaron) in a nanowire that is subjected to an ultrafast optical pulse.

During this past year, we noticed that our previous research results on AuGa-catalyzed nanowire growth showed that we can enhance the abruptness of the SiGe heterointerface inside a single nanowire heterostructure. However, local electrode atom probe tomography (LEAP) and HRTEM studies revealed unintentional Ga incorporation inside the Si(Ge) nanowire resulting in dopant compensation due to the 3+ valence state of Ga. To eliminate this spurious doping effect of Ga inside the group-IV nanowires, other alloys, such as AuSn, will be employed as an alternative catalyst for VLS nanowire growth.

Our studies of Si radial shell growth revealed several novel observations in nanoscale epitaxy, such as the critical thickness of P-doped Si shells and the diameter-dependent radial growth rate. Radial epitaxy is a new research direction closely related to device applications as 3D-architectured nanodevices become more prevalent. Comprehensive studies of radial epitaxy will open new areas of material preparation on curved surfaces.

3D devices require well-defined morphology and vertical alignment for both accurate design of device performance and facile fabrication. Though nanowires are ideal building blocks for 3D devices, vertical alignment of nanowires has been only achieved under strict growth conditions. For instance, vertically aligned Si nanowires can be grown only by a combination of high growth temperature (1000 ºC) and a corrosive precursor ($SiCl_4$). As a general method to grow vertical semiconductor nanowires, confined epitaxy – the growth of nanowires inside spatially-defined cavities or holes – will be studied. We have already demonstrated the growth of Si nanowires using anodized aluminum oxide (AAO) as a growth template. We will expand this concept for the control of diameter, length, and spacing of nanowires with other types of templates such as hole-patterned dielectric layers.

A combination of semiconductor nanowires and 2D layered materials can have versatile functionality for flexible devices. Graphene, a well-known 2D layered material, has been used as a base material for flexible electronics and photonics. Generally, graphene acts as the electrode, not the active material, in flexible devices due to its high electrical conductivity and absence of a band gap. Other 2D layered materials with band gaps, such as $MoS_2$ and $WS_2$, could substitute for graphene as the base of flexible devices to exploit the properties of heterojunctions between the semiconductor nanowires and the 2D material. The epitaxial growth of nanowires on 2D layered materials is an interesting science topic in its own right because crystalline nanowires can be grown by van der Waals forces and not the traditional chemical-bond structural relation between the growing material and the substrate.

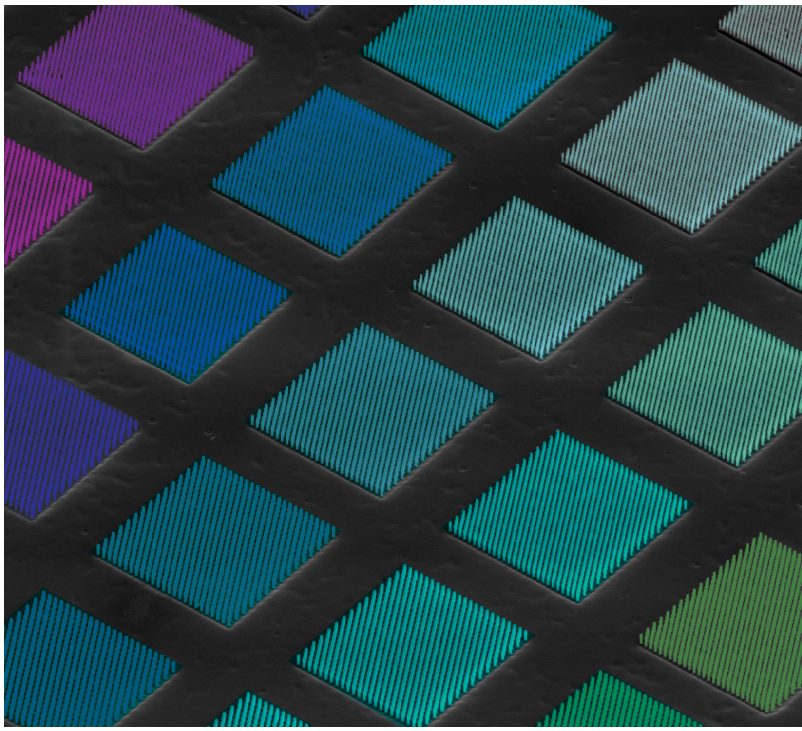


Figure 8: These are arrays of nanowire (GaN/InGaN) photonic crystals. Each "patch" is a small photonic crystal, and the reason they are colored differently is that each one lases at a different wavelength.

## Metamaterials and Plasmonics

(a) Sample

(b) Generalized Refraction

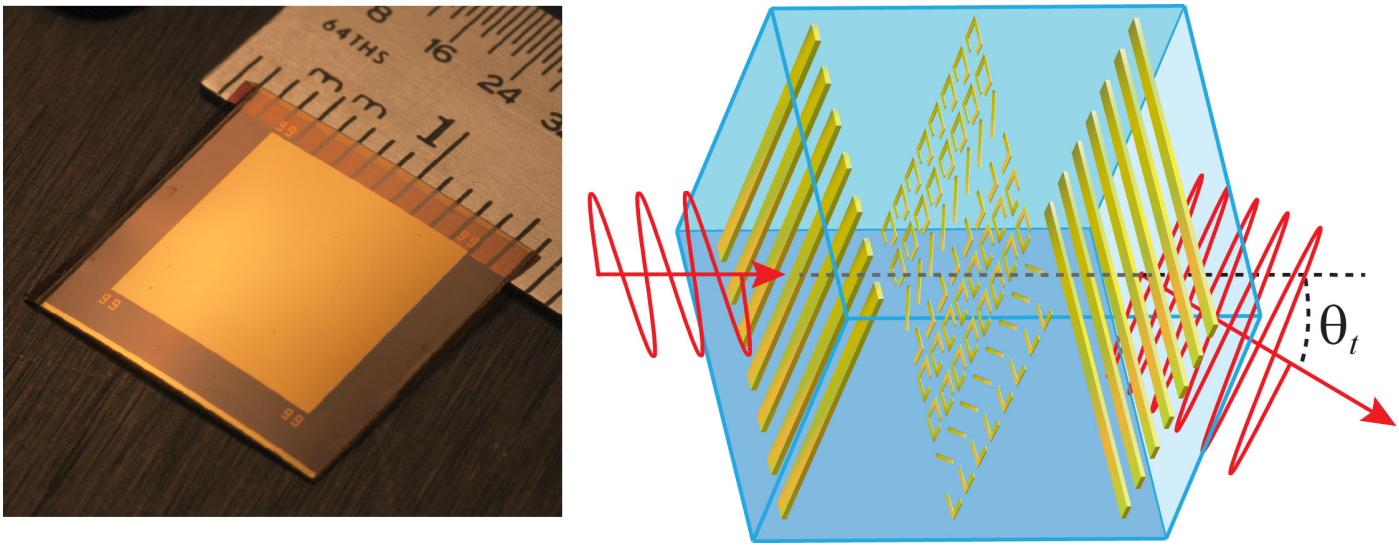



Figure 9: (a) Photograph of an ultrathin (72 μm thick) metamaterial sample. (b) Illustration of how the metamaterial redirects an electromagnetic wave, which would not happen for a normal thin film. The structure is not drawn to scale.

Artificially structured metamaterials and plasmonics provide novel properties that are difficult or impossible to achieve using naturally occurring materials. The new class of electromagnetic artificial materials greatly extends our ability to manipulate electromagnetic radiation (light), and has led to the demonstration of unique behavior such as negative refraction, cloaking, and superlensing. The Metamaterials and Plasmonics Integration Focus Activity builds upon the extensive activities at CINT in this field over the past few years spanning from terahertz to optical wavelengths. The goals of these activities are to understand and design metamaterial and plasmonic structures capable of enhanced interactions with light, and to accomplish novel functionalities from tunable and nonlinear hybrid metamaterials through integration of semiconducting and/or complex oxide materials and structures. During the past years CINT has demonstrated leadership in this field through the groundbreaking work in novel metamaterial structures, active and dynamical metamaterials and plasmonics, and their applications to sensing and imaging.

Recent progress in this IFA has been made in the following areas.

*Plasmonic manipulation of photon emission properties in optical nanomaterials*

We have ventured into the realm of multi-exciton-MN interactions by performing systematic PL and photon-correlation spectroscopy studies at room temperature and 4K. Our study revealed that:

1. photon antibunching of individual nanocrystal quantum dots (NQDs) can be transformed into photon bunching when they are coupled to MNs;
2. manifestation of this novel phenomenon required to metal-induced PL quenching with a rate that scales more slowly with exciton multiplicity than the radiative decay rate and dominates over other nonradiative decay channels for both single excitons and biexcitons;
3. strong enhancement in absorption is not necessary for a strong multiexciton emission; and
4. the enhancement to the emission of MX gets stronger with the increase of multi-exciton order.

*Photonic density of states enhancement from subwavelength metal-dielectric film structures*

Recently the surface plasmon polariton frequency range can be tuned to a wide frequency range (from 0.5 -1.8 um) using alternating layers of thin metal(Au) and dielectric ($SiO_2$) films known as hyperbolic metamaterial. Wider tuning range is possible (infrared and mid-infrared) using highly doped semiconductor and ITO. We have explicitly demonstrated tunability in the near-infrared by measuring the SPP dispersion curves of three samples with different $SiO_2$ thicknesses. The remarkable aspect of this structure is that with merely two and half periods the dielectric properties can be described adequately using effective medium approximation. Because the fabrication of this deeply subwavelength nanostructure is rather simple, this can serve as a plasmonic platform for integrating quantum dot emitters.

*Strong-coupling between metamaterials and dipolar transitions: optical phonons and intersubband transitions in semiconductor heterostructures*

We have been exploring the interaction between metamaterial resonators and various dipole resonances with the aim to study the "ultrastrong" coupling regime (when the Rabi frequency approaches the dipole frequency) and to provide for new ways for tuning of metamaterials. As an example, infrared phonons in dielectrics (such as $SiO_2$) placed in proximity with metamaterial resonators can couple strongly, leading to normal mode splitting similar to vacuum-Rabi splitting that occurs with optical emitters coupled to microcavities. The amount of coupling can be altered through the design of the metamaterial resonators, the proximity of the dielectric layer to the resonator, the dielectric film thickness, and the amount of field overlap with the

dielectric layer. Strong dipole transitions can be engineered using intersubband transitions (IST) in semiconductor heterostructures. We have demonstrated this for the case where both structures, the MM and ISTs, were optimized for maximum interaction. The MM rotates the incoming polarization in the near-field making it compatible with the IST selection rules. When the metamaterial resonance and quantum-well transition overlap, the two lines anti-cross with a characteristic splitting of ~3.6 THz, corresponding to 15% of the central frequency. This regime corresponds to "ultra-strong" coupling and we verified the energy exchange between the resonator and the IST in the time domain by measuring the amplitude and phase of a reflected pulse at 10mm using a new phase-locked time-domain spectroscopy system.

*Metamaterials for antireflection coating, perfect absorption, polarization conversion, and anomalous refraction*

We have demonstrated ultrathin planar metamaterials for a host of functionalities:

1. Antireflection coatings on highly reflective substrate (GaAs), which dramatically reduce reflection from 32% to 0.1% and enhance transmission from 68% to 90%.
2. Narrowband and broadband near-unity absorption by simultaneously minimizing the transmission.
3. High performance and ultra-broadband linear polarization converters in either reflection or transmission mode.
4. Near-perfect anomalous reflection/refraction by creating a linear phase gradient, which paves the way towards the development of a class of next generation thin-film-like flat photonic elements.

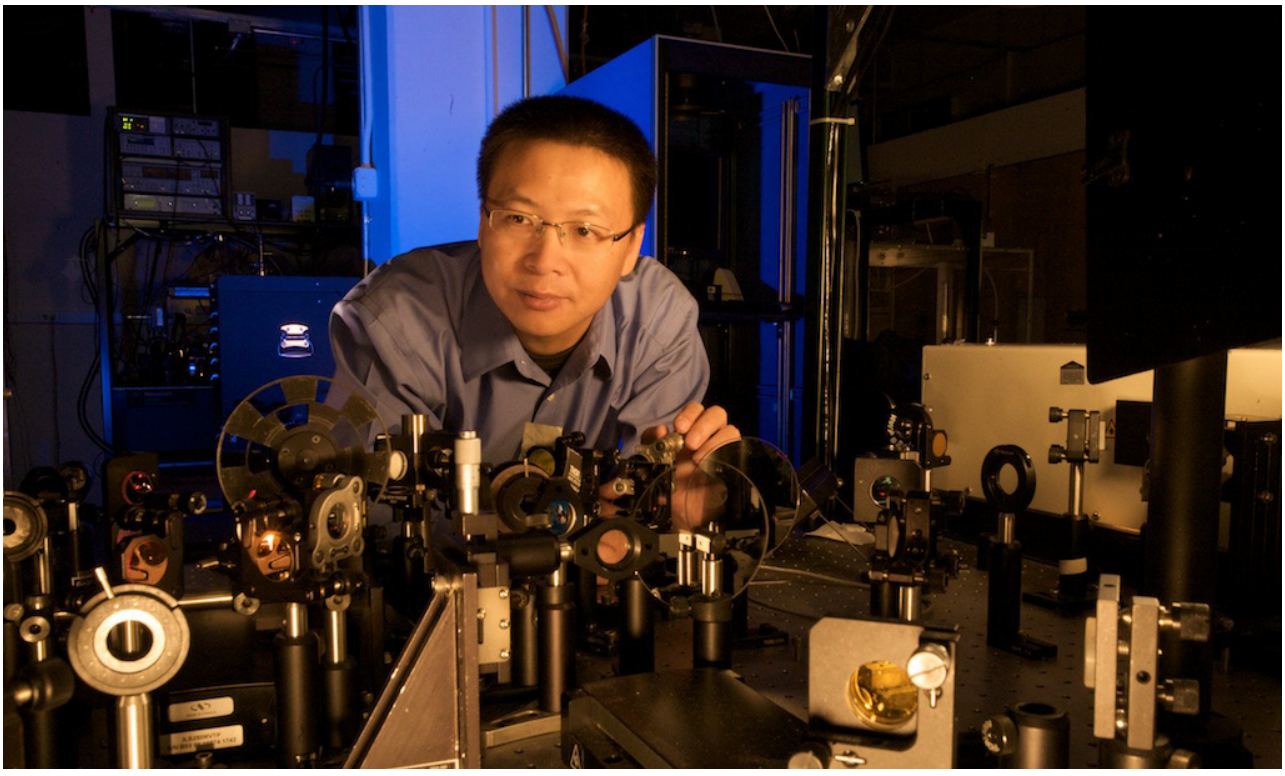
These metamaterials are fabrication-friendly and use only regular metal and dielectric materials with no demanding requirements of material properties and thickness.

*Active metamaterials*

We have developed a host of active metamaterials by integrating functional materials and applying external stimuli:

1. Using $SrTiO_3$ (STO) as the metamaterial substrate we accomplished continuous thermal tuning of resonance frequency over one octave, due to its temperature-dependent dielectric constant increasing from $\varepsilon$~200 at 400 K to $\varepsilon$~1000 at 150 K.
2. Integrating semiconducting materials (silicon) at the critical regions of metamaterial elements we demonstrated switchable metamaterial-based classical analogue of electromagnetically induced transparency (EIT) through optical excitation, and switchable meta-molecule chirality.
3. We demonstrated tunable and strong nonlinear resonant response in high-temperature superconducting metamaterials, where metal was replaced by YBCO films.

We discovered that the resonance is strongly dependent on nanoscale YBCO film thickness, temperature, photoexcitation fluence, and incident field strength. We established a theoretical model and found that the kinetic inductance and surface resistance are responsible for the observed tunable and nonlinear MM response.



HouTong Chen, one of the CINT Scientists leading the Metamaterials IFA.

# Scientist Profiles

## Rohit Prasankumar

*Lighting the way with lasers*

Rohit Prasankumar doesn't work in a dance club; he leads several optical research laboratories. His approach to studying complex materials, however, is similar to how a club's strobe light illuminates and freeze-frames dancers, making it appear as if slices of time stand still. At the Center of Integrated Nanotechnologies, he designed laser systems that produce a strobe light effect. They strike a material with short optical pulses, producing snapshots at less than a trillionth of a second. "Rohit is a very inventive instrumentation scientist," CINT Director David Morris said.

Ultrafast microscopy is just one unique capability that Prasankumar has developed at CINT, a Department of Energy nanoscale science research center jointly operated by Los Alamos and Sandia National Laboratories. His research at the national user facility builds upon work he began in college. As an undergraduate student in electrical engineering at the University of Texas at Austin, Prasankumar used lasers to look at human tissues, and in the process became intrigued with laser physics. However, his graduate institution, the Massachusetts Institute of Technology (MIT), didn't have an applied physics program so he enrolled in as many physics courses as he could, focusing his research on ultrafast optics and ultrafast phenomena.

"A lot of things happen too fast to be measured with electronics," he said. For his doctoral thesis, he designed and built novel ultrashort, pulsed lasers with performance on par with conventional ultrafast titanium-sapphire crystal lasers, at a fraction of the cost.

In 2003, after MIT, Prasankumar headed straight for Los Alamos and CINT, which, he said, is one of the few research institutions where scientists who grow new kinds of materials interact with theorists and experimentalists who characterize those samples using advanced laser-based techniques. "We're really trying to understand the properties of complex materials at a very fundamental level," he said. "If there's an experiment you can imagine, there's a good chance we can do it." To study a nanowire in both time and space, for instance, Prasankumar and his colleagues developed a method to focus light pulses through a microscope and record time-resolved images, the results providing scientists a unique look at newly emerging phenomena.

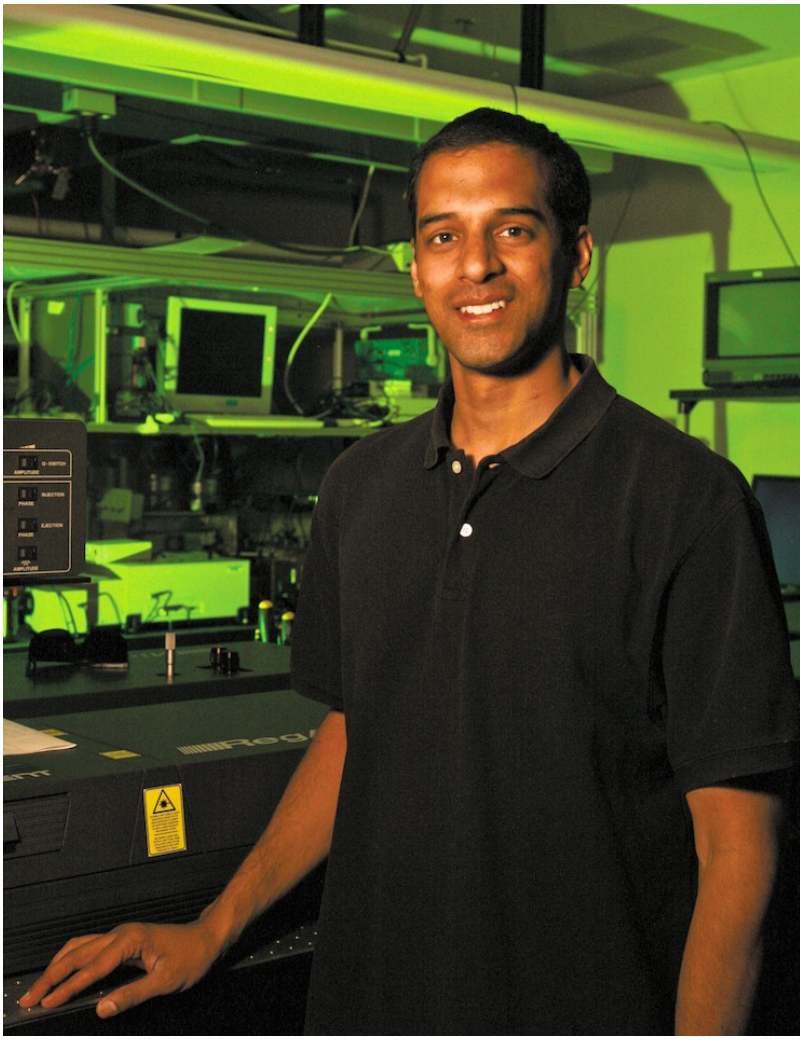
***Managing science brings new momentum***

In less than six years at CINT, Prasankumar has gone from being a postdoctoral researcher to recruiting and directing them. From his base at the CINT Core facility in Albuquerque, where he supervises two postdoctoral researchers, he travels weekly to Los Alamos to advise three postdoctoral researchers. He oversees labs at both sites as they carry out research using experimental systems he helped design. He is a reviewer for numerous scientific journals and recently co-edited a book with MPA Division Leader Toni Taylor, a pioneer in terahertz science and technology who mentored him as a postdoctoral researcher. *Optical Techniques for Materials Characterization*, published in 2011, also includes a chapter he co-wrote with Taylor on emerging optical techniques.

As a staff member of a national user facility that attracts hundreds of projects each year, Prasankumar also guides CINT users as they perform ultrafast spectroscopy over an ultraviolet-to-terahertz frequency range. "We are fortunate to have many outstanding scientists from different universities and government labs who are interested in collaborating with CINT, which enables us to produce high-quality science and explore new scientific directions," he said.

Prasankumar said he is involved with 10 to 20 projects a year, spanning a wide range of science—from ultrafast dynamics in semiconductor nanostructures and correlated electron materials, to organic interface layers used in solar cells and negative refraction in optical metamaterials and plasmonic devices.

"Rohit fills a very special niche in our nanophotonics and optical nanomaterials thrust in the Center for Integrated Nanotechnologies," said Morris. "He is a truly first-rate ultrafast spectroscopist, and he has a tremendous grasp of condensed matter physics. This combination enables him to address some of the most interesting and challenging problems in functional nanomaterials, as well as attract CINT users from some of the very best research institutions in the world."



Rohit Prasankumar

# Judith Driscoll and Quanxi Jia

***Crossing an Ocean for Collaboration on Multifunctional Thin Films***

Several times a year, Judith Driscoll crosses the Atlantic Ocean to visit CINT. What makes her 11,000-mile round trip from the University of Cambridge worth it?

"People, principally," says Driscoll. She endures the long travel from England for the rewarding scientific collaborations with the people here. At CINT, collaborations, like her decades-long work with CINT scientist Quanxi Jia, lead to innovation.

Driscoll breaks from her role as a Professor of Materials Science at Cambridge to visit LANL and conduct research with Jia, staff scientist and Nanoscale Electronics and Mechanics Thrust Leader at CINT. As a team, Driscoll and Jia have been researching electronic thin films for nearly two decades.

Less than a micron thick, or approximately 100 times thinner than a human hair, thin films can be deposited by different coating technologies. Depending on their physical properties, the thin films have an array of applications, ranging from electronics to thin film optics to energy harvesting.

"I got into thin films when I was a postdoc at Stanford," says Driscoll. "Thin films were needed for studies to understand about fundamental physical properties of superconductors."

Together, Driscoll and Jia have investigated a wide range of metal-oxide thin films deposited by a process of pulsed laser deposition (PLD). Ultimately, these thin films have the whole range of electronic properties from superconducting to insulating, with almost everything else in between, including semiconducting, ferroelectric, and magnetic. These properties depend on their precise thickness (10–1,000 nm), composition, and method of formation.

Currently, Driscoll and Jia dedicate time to research such things as multiferroic bismuth ferrite ($BiFeO_3$). "By growing ultrahigh quality thin films of different kinds," says Driscoll, "we have been able to tune the magnetic and ferroelectric properties of $BiFeO_3$ in amazing ways to give it much better performance and real potential to act as a room-temperature-operating magnetoelectric material."

These materials can be used to develop new electronic devices for computer memory and processing. Other complex oxide thin films extensively investigated by Driscoll and Jia can be used in mobile communications devices, semiconductor processors, and even energy harvesting components.

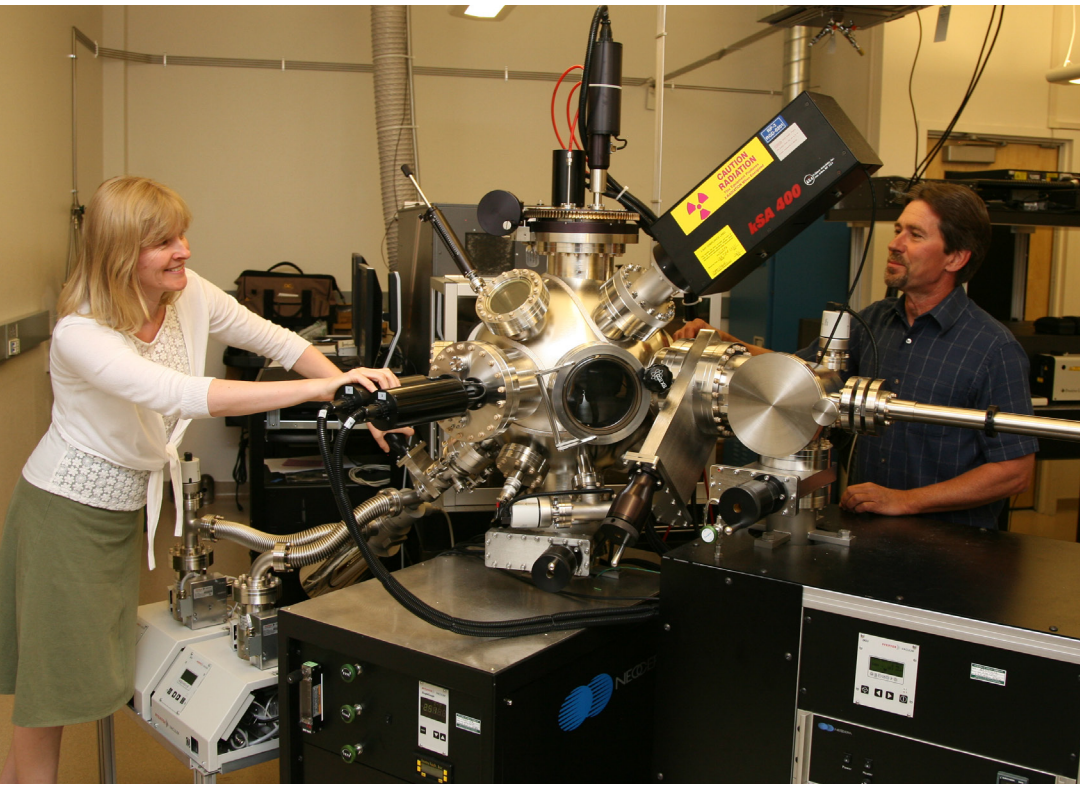
Driscoll and Jia's work together has resulted in numerous publications in prominent scientific journals and through patents, which benefit both the Laboratory and the growing field of materials science. Another critical team member helping them is Paul Dowden, an instrument technician who has worked consistently with Driscoll and Jia since 1995.

Such successful collaboration requires "know-how" and trust, and this team has cultivated nearly two decades of it.

Collaboration helps keep minds open, says Driscoll, who is also the editor of *APL Materials*, a new open access materials science journal published by the American Institute of Physics. "I think it is very important not to focus on only hot topic areas which promise predicted results and high-impact journal articles, but simply on funding good people to do exploratory, open-ended, curiosity-driven research."

"Research is thinking," says Jia. "It is a team effort when we generate and discuss ideas." The most important part of science, he stresses, happens before entering a laboratory.

As Driscoll returns to Cambridge, she won't allow the Atlantic to stop her collaboration with Jia. Rather, she will continue to research multifunctional thin films in preparation for her next trip to CINT, because the people here make crossing an ocean worth it.




CINT User Judith Driscoll and Technologist Paul Dowden

## Amalie Frischknecht

Beyond Amalie Frischknecht's pleasant, light-filled office in CINT, a lively sparrow hops on an outside window ledge. She says to her visitor, "CINT is one of the best places to do research at Sandia."

One might be deceived by her unalloyed pleasure in her location into thinking she was just starting out. Then she gives a more practical reason for her happiness: "If we're doing good research with a CINT user, there's no particular reason to stop work on an interesting project after only two or three years and propose something entirely different."

A check of her resume shows that extended periods of concentration and collaboration on particular subjects aren't just a naïve hope for Amalie but an accomplished fact. The theoretical physicist, who graduated with her Ph.D. from UC Santa Barbara in 1998, has given 32 invited talks and published 49 papers, almost all on fundamental aspects of a subject she obviously has been considering for many years: polymer physics.

"I find it easier to wrap my brain around molecular phenomena rather than, say, quantum physics," she said. "Polymer physics is a very large field and I've looked at a subset of it, based on what Sandia is interested in and where I can find collaborators. I have pursued polymer physics for most of my professional life."

But rather than relentlessly investigate one aspect of her field, she feels more comfortable working in a garden of ideas. Which ideas germinate depend on two factors: is there the money to water a particular seed, allowing time to pursue it further, and is there an interested experimentalist who can move forward with her?

She provides models for experimentalists to test, and sometimes her simulations provide physical insights that experimentalists with the best equipment can't find.

A number of plants in her garden show signs of flowering. With Karen Winey - a CINT user and researcher at the University of Pennsylvania - Amalie is attempting to find a better substitute for the solvent ethylene carbonate used in lithium batteries.

"Ethylene carbonate is a good conductor, but it's flammable," she says. "People would like instead to use ionomers - polymers with ions attached to them. We know that though they are poor conductors, they're safe. The question to us is how to make them better conductors."

Discussing matters with Winey at conferences over the years since 2008 - mostly the APS March meeting and the Gordon Conference on polymers - Amalie applied for and received an LDRD in FY2010 entitled, "Ion Transport in Ionomers for Energy Storage." The LDRD allowed a team of Sandia staff and postdocs to investigate the ionic clusters in ionomers in detail.

"It was thought that negative ions attached to the polymer tend to cluster with the positive lithium ions, and these clusters could reduce the charge-carrying capacity of the polymer," she says. "We asked: if we modify the shape of the polymer, how does that affect the clustering that takes place between the negative and positive ions?"

The positive ion may sit on the negative ion like a rider on a horse and move "slowly like molasses," she says. Or the negative ions may function with the positive ones like a roller derby team, passing them forward, a much more rapid process. The question is, "can you design the polymer to speed up the process? Do you space it with 10 carbons or 100? Space it further off the backbone? Or use a different kind of polymer?"

Each simulation of a new polymer shape takes a couple of months on Sandia's Red Sky supercomputer, using 16 to 32 processors. So it took about two years to identify the characteristics of 22 polymer variations.

Among other results, the work should end a controversy over the shape of the ionic aggregates in the ionomers. "People thought that the ionic aggregates in ionomers were spherical. We've shown that they tend to be stringy-shaped. When you're trying to understand the mechanism of how lithium ions move along a polymer, the shape of these clusters clearly would influence that movement. A stringy ionic aggregate can move ions better."

Amalie won an Employee Recognition Award for leading this work, which was first published in Physical Review Letters, with follow-on work by the team published in four other journals. Further research on ionomers is continuing as a CINT user project. "We're working on 3 more papers right now," says Amalie.

A second project she's pursued since 2007 involves making stable dispersions of gold nanorods in a polymer film. "We don't want the rods to clump up as we grow the film." Amalie and CINT user Russell Composto, also from the University of Pennsylvania, believe that such a film could have "nice optical properties, if we could control the spacing of the gold nanorods." The film, used as a sensor, could alter the resonant frequencies of light passing through it if a particle landed between the rods.

"Years ago, I did some calculations that were interesting to Russ, about nanorods in polymers. He was actually doing it. We said, 'Let's work together.'"

Amalie Frischknecht

# User Program

The CINT user program is designed to provide the international scientific community access to Core and Gateway Facilities. User access can include use of capabilities in either or both of our Facilities as well as engagement of the CINT Scientist staff expertise. There are two modes of user access: General User access and Partner User access, each with variable scope and the ability to conduct nonproprietary or proprietary research.

CINT users may conduct their approved research projects in collaboration with one or more CINT Scientists or may choose to access CINT capabilities independently. User proposals are evaluated on the merits of the science without preference for collaborative/independent access.

Users working independently are properly trained and supervised by technical personnel. Some CINT capabilities cannot be operated independently for safety or complexity reasons.

User proposals consist of a 2-page (maximum) pdf document that is uploaded via the website along with user information entered on-line. All user proposals undergo an initial feasibility/safety screening by CINT technical staff, and a technical peer-review conducted by external Proposal Review Panels that reflect the four CINT Scientific Thrusts. The CINT Management uses the Review Panel scores and comments to prioritize access to CINT.

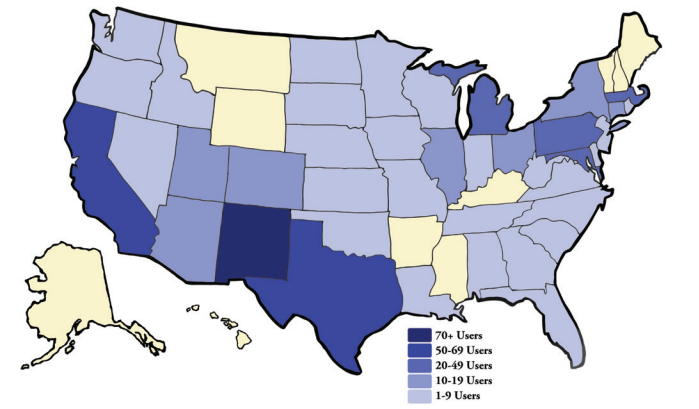



Figure 10: In 2012 CINT Accepted 189 user projects. CINT hosted 356 users from 32 of the 50 States and 21 Foreign Countries.

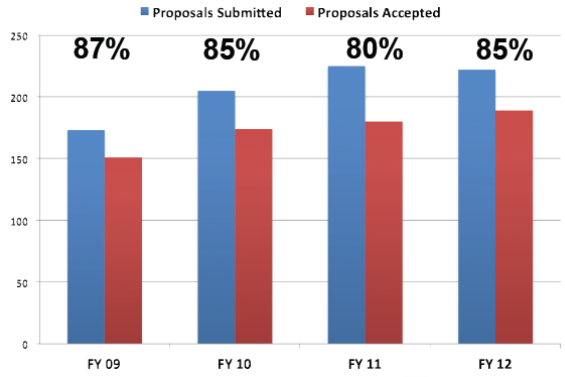



Figure 11: Proposals submitted to CINT are often very high quality, leading to a high acceptance rate.

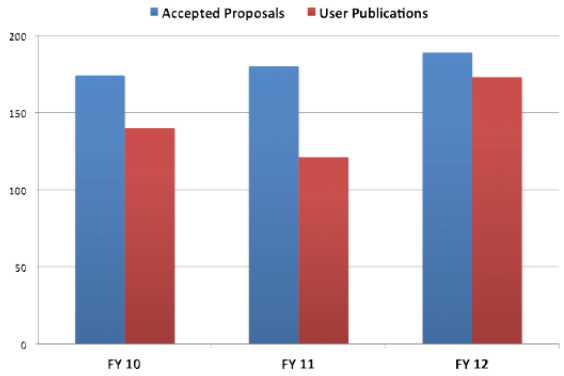



Figure 12: Our focus is on high-impact projects, leading to a 1:1 correlation of projects to publications.

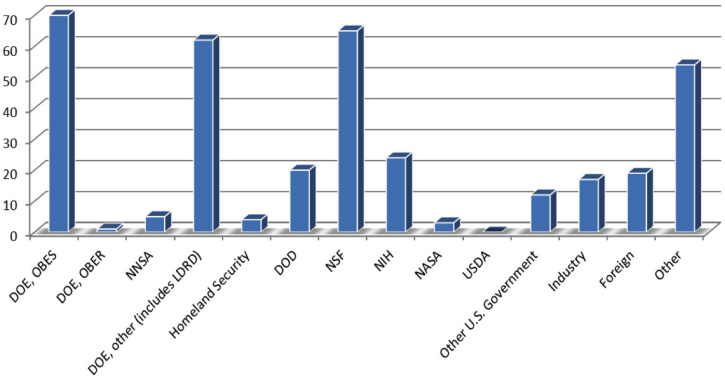



Figure 13: Source of support for user projects comes from a wide variety of agencies and instutions.

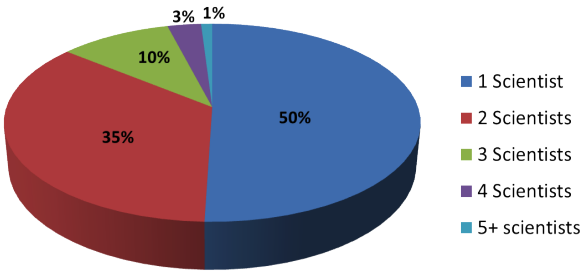



Figure 14: Approximately half of proposals submitted ask for collaborations with more than one CINT scientist.

# 2012 CINT Users Conference

CINT held its 12th Annual Users Conference on September 18th-20th, 2012 at the Albuquerque Marriott Hotel in Albuquerque, New Mexico. There were 173 registered participants from 40 Universities, 5 Industries, and 7 Government Agencies and Laboratories.

Three plenary presentations opened up the Conference beginning with Charles Lieber (Harvard University) who gave a presentation on *Nanowires, Nanoscience and Emerging Technologies*. Oskar Painter (California Institute of Technology) then spoke on Chip-*Scape Optomechanics: Towards Quantum Light and Sound*; followed by Vicki Colvin (Rice University) who discussed *The Nano-bio Interface Applications and Implications*. Continuing with our tradition of science symposia around active areas of user projects and research at CINT, three concurrent symposia were held during the event.

1. Advances at the Interface of Biology and Nanomaterials [*Organizers: Linda Peteanu & Elba Serrano (UEC) Jennifer Hollingsworth, George Bachand, Gabe Montano (CINT)]*;
2. NanoMechanics of Top Down and Bottom Up Nanostructures [*Organizers: Guillaume Gervais & Dvora Perahia (UEC) Mike Lilly & Nate Mara (CINT)]*; and
3. Nanowires [*Organizers: Suneel Kodambaka & Eric Shaner (UEC) Stuart Trugman & Brian Swartzentruber (CINT)]* . A Poster Session with contributions from Users and CINT scientists was held, as well as an optional tour of the Core facility.

The Advances at the Interface of Biology and Nanomaterials Symposium focused on the application of nanomaterials and nanoscale design concepts to biology, as well as the converse – bringing biological principles and even "biomaterials" to bear on nanomaterials development. The interface between the truly biological and the "artificial" was viewed as a frontier area because of the promise for emergent and unexpected properties resulting from new hybrid bio-inorganic/organic or bio-inspired materials and assemblies. The Symposium also provided an opportunity for "bio-functional" (e.g., imaging agents, nanodrugs) but purely "non-biological" nanomaterials to be discussed toward understanding the role that such materials can play on their own or as part of more complex systems or devices in impacting questions of health or biosecurity. In so doing, the represented topics spanned the range from simple constructs to complex "nano-biomachines" and assemblies. Though not the explicit focus, clear application themes developed in imaging, diagnostics/sensing and therapeutics. The Symposium also considered the often neglected but critical questions of biocompatibility and sustainability.

The Nano Mechanics of Top Down and Bottom Up Nanostructures Symposium, encompassed two limits ofnanomechanics: that of nano structures engraved in matter (Top Down) and that of assembled nanoparticles (Bottom Up).

1. Lithographic or top-down nano structures that are often "test beds" for predictions of quantum mechanics will be discussed. They have an immense technological potential from innovative biosensors and new frequency standards for electronics to quantum information and quantum control. Understanding nano-mechanical resonators and their dissipation modes for example could lead topowerful and sensitive tools for biological and chemical sensing, whereas Nano Electro Opto Mechanical Systems will impact quantum information and quantum control.
2. The nanomechanics of assembled nanoparticles or bottom up assemblies that advance the development of Programmable Membrane Based Nanocomposites was discussed. The nanomechanics of nanoparticles integrated into polymer brushes for example affect plasmonic, electronic and magnetic coupling between the particles. Understanding the nanomechanics of polymer mediated nanoparticles assemblies will result in formation of ultrathin, highly flexible yet strong two dimension thin responsive membranes.

The Nanowires Symposium, focused on topics ranging from nanowire synthesis, characterization, to fabrication and testing of devices. Nanowires, high aspect ratio crystalline structures whose surface as well as bulk chemistry, crystallinity, and morphology can, in principle, be controlled with atomic-level precision, have attracted a lot of attention over the past decade for a variety of applications including nanoelectronics, optoelectronics, energy storage and harvesting, catalysis, and biosensors.

The Conference was preceded by an on-site focused Industrial Outreach Session hosted at the CINT Core facility in Albuquerque.

CINT's Industrial Open House attracted participants from small businesses around the state. This workshop was specifically targeted to scientists and small business owners of technology companies in the private sector (industry, small business, start-ups, etc.). Speakers included CINT user and Senior Industrial Advisor, Ed Flynn (Senior Scientific) and CINT user Spencer Farr (Vista therapeutics). The talks described various models for interacting with the Sandia and Los Alamos National Laboratories and highlighted scientific successes of the companies in their collaborations with CINT. Several small businesses requested follow up meetings with CINT scientists as a result of the session.

# Nanophotonics and Optical Nanomaterials Thrust

**Igal Brener, Thrust Leader; Jennifer Hollinsgworth, Acting Partner Science Leader**

The Nanophotonics and Optical Nanomaterials thrust seeks to address the overall scientific challenge of understanding and controlling fundamental photonic, electronic and magnetic interactions in nanostructured optical materials fabricated using both chemical and physical synthesis. Major thrust research activities can be classified into four themes:

1. Spectroscopic investigations into the properties of novel 0D, 1D, and 2D optical and magnetic nanomaterials from the level of single nanostructures to ensemble behavior;
2. Development of new characterization tools;
3. Development of new optical nanomaterials; and
4. Materials integration toward emergent phenomena (metamaterials, coupled optical-plasmonic materials) and/or enhanced device-level performance.

**Recent Accomplishments:** Significant progress in the past year has been made in the areas of synthesis of low-dimensional materials, incorporation of these materials into functional devices, optical spectroscopy capability development and application to low-dimensional materials, and studies of 1- and 2-D carbon nanomaterials.

**Synthesis of Low Dimensional Nanostructures**:

*(a) Improvement of photovoltaic material processability*

Recent successes in the synthesis of chalcogen-based photovoltaic (PV) nanomaterials – Cu(In,Ga)$S_2$ (CIGS), $Cu_xZn_{1-x}Te_yS_{1-y}$ (CZTS), and $FeS_2$ – translate into the need of better material processability and the ability of their incorporation into a conductive matrix for low-cost PV film depositions. To address the new processing challenges we studied the alternative means of particle passivation replacing the organic thiols with inorganic alternatives – simple and complex sulfides: $(NH_4)_2S$, EtNCS, $Sn2S_6^{4-}$ and $SnS_4^{2-}$. The replacement of organic thiols results in complete elimination of carbon from the surface of protected nanoparticles significantly improving the inter-grain contacts in pyrolitically deposited thin films of CIGS and CZTS materials. The introduction of strongly-binding sulfides is also expected to decrease the density of trap states on the surface of $FeS_2$ particles by restoring the octahedral environment around each surface iron.

*(b) Development of new nanomaterials for optical and magneto-optical applications*.

We have focused in two concerted directions: the synthesis of type-II ZnTe/ZnSe core/shell nanorods to advance the understanding of charge polarization and separation in anisotropic nanostructures and the development of synthetic approaches to magneto-optical materials. The reproducible and efficient synthesis of ZnTe nanorods has been achieved and different approaches for the ZnSe shell deposition have been tested out. In the area of magneto-optical nanomaterials, we focused on the development of synthetic strategies for InSb/MnSb core/shell nanoparticles, where semiconducting InSb material with narrow and direct band gap is coupled with ferromagnetic MnSb.

*(c) Understanding of electronic structure of optical nanomaterials*

To gain insights into electronic structures of luminescent species, we studied the local environment influence (the type of protecting ligand and nature of the solvent) on the absorption properties of small CdSe nanocrystal conventional type-I semiconductor nanocrystals and the nature and structure of molecular-size noble metal clusters. The latter are increasingly important in biological applications as much smaller and more benign alternative to the former.

*(d) New synthetic methods for novel complex optical nanomaterials*

We transformed the solution-liquid-solid (SLS) method of semiconductor nanowire (SC-NW) synthesis into a flow-enabled technique ("flow" SLS, FSLS) with the resulting synthetic control affording unprecedented mechanistic insight and a platform for designed synthesis of technologically significant axially heterostructured SC-NWs. SLS SC-NWs are high quality candidates as next-generation nanoscale "building blocks" for nano-enabled optoelectronics and energy harvesting

*(e) Beyond the fundamentals: Device platforms for evaluating nano-to-mesoscale performance and bio-impact*

We have demonstrated the unique attributes of g-NQDs for light-emission applications. First, we fabricated light-emitting diodes with NQD monolayers as the emitting layer excited by direct charge injection. Second, we showed the potential for g-NQDs as replacement down-conversion phosphors due to their chemical/ photostability, color-purity and minimal self-reabsorption losses (large "effective" Stoke shift). Even more recently, we extended the utility of our materials to 3-D single-particle tracking in live cells, demonstrating a 20-fold enhancement in average tracking time compared to standard NQDs.

**Optical Spectroscopy of Low-Dimensional Nanostructures:**

*(a) Single nanostructure optical spectroscopy for understanding the competition between radiative and nonradiative recombination processes in optical nanomaterials.*

We have conducted a series of single nanostructure optical spectroscopy studies (including a new single NQD spectroelectrochemical approach) to understand (1) mechanisms responsible for suppression of Auger process, (2) the role of Auger processs and charging in PL blinking of NQDs, and (3) the influence of electronic structure and energy band alignment on suppression of blinking and Auger processes. Specifically, we have applied two novel single NC spectroscopy techniques to study how the emission. We have also developed new spectroscopic approaches to disentangle the effect of clustering and MX emission in 2$^{nd}$ order photon correlation experiments. These approaches will play critical role in study of mesoscopic nanomaterial assemblies. We have also developed simultaneous optical and electrical characterization capability to probe competition between separation and recombination in single Si nanowire photovoltaic cell.

*(b) Mapping carrier diffusion in single Si core–shell nanowires with ultrafast optical microscopy*

To optimize device performance in heterostructured nanowire applications, it is especially important to understand the influence of interfaces on charge transport in these quasi-one dimensional (1D) systems. We used ultrafast optical microscopy to directly examine carrier dynamics and diffusion currents in both single silicon (Si) core and Si/$SiO_2$ core/shell NWs with high spatial and temporal resolution in a non-contact manner. A striking difference in carrier dynamics and diffusion current maps was observed for Si NWs with or without $SiO_2$, due to trapping in unpassivated surface states.

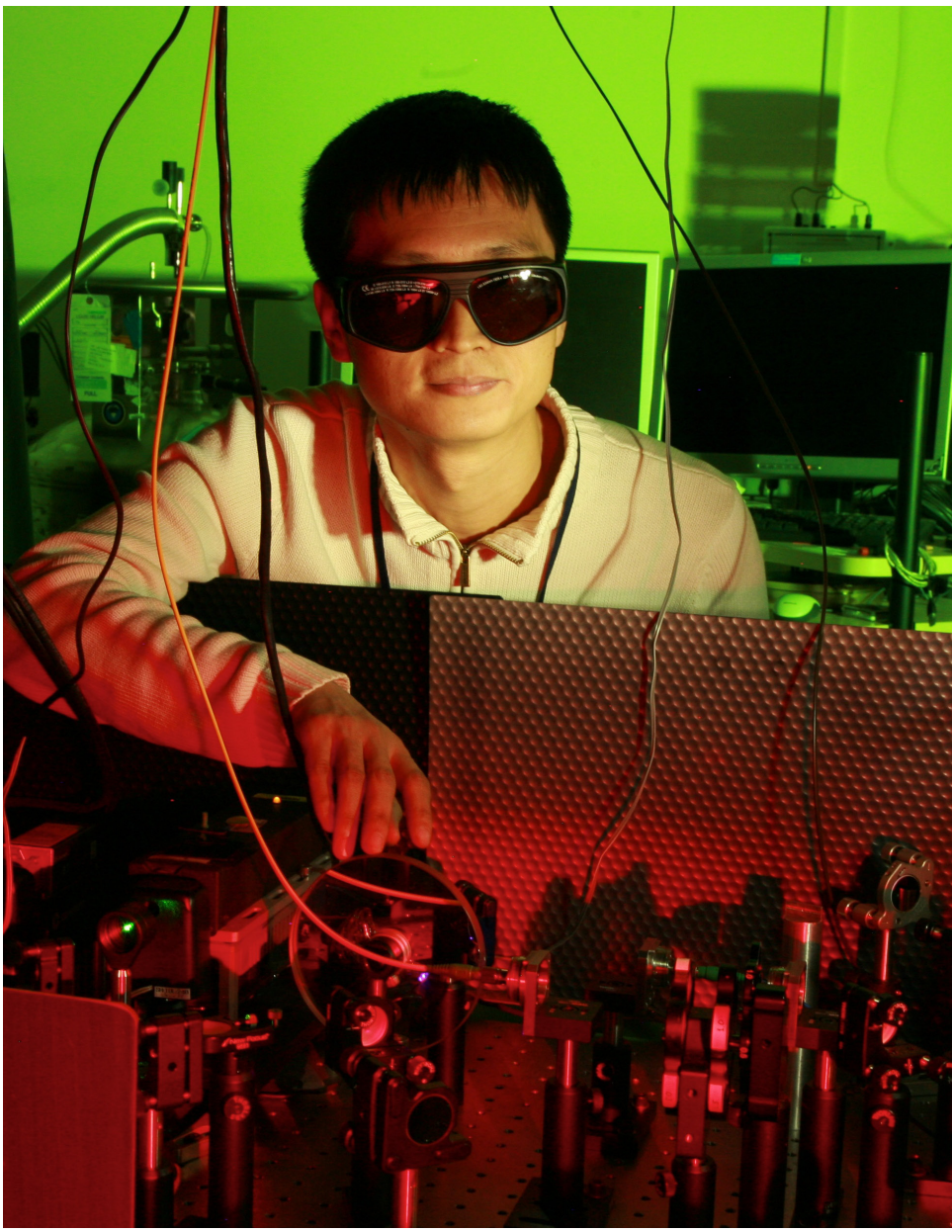
*(c) Photoinduced stabilization and enhancement of the ferroelectric polarization in $Ba_{0.1}Sr_{0.9}TiO_3$ / $La_{0.7}Sr_{0.3}MnO_3$ heterostructures*

The variety of applications for ferroelectric (FE) materials has motivated many studies aimed at increasing the FE polarization and its transition temperature $T_c$. We demonstrated that optically pumping carriers across the interface between a thin film of the canonical FE insulator $Ba_xSr_{1-x}TiO_3$ (BSTO) and the ferromagnetic metal $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) can significantly enhance the FE polarization in BSTO, as detected through second harmonic generation (SHG) experiments due to charge confinement and separation in the heterostructure, causing the photoexcited carriers to screen the internal depolarizing electric field.

**Carbon-based nanomaterials: Nanotubes and Graphene:**

Through development of new optical probes of interfacial structures we have enhanced understanding of surfactant structure and the ability to manipulate it. This has enabled our recent development of silica-based aerogel composite materials that retain the nanotube PL. The composites are enabling user projects on multi-component interactions, development of optical cavities, their use as a matrix for studying fundamental exciton behaviors, and studies on the templating role of nanotubes for generating longer-range mesostructures. We have also pushed our studies of 1-D surface chemistry to the single-tube and even single-dopant site level, revealing the electronic nature of different dopant types and demonstrating for the first time the surface mobility of dopant species. Single tube imaging has also given us the first direct measurement of exciton diffusion lengths, that when paired with single tube lifetimes and spectral widths have allowed evaluation of mechanisms for exciton motion. Single tube PL lifetime measurements have also recently revealed the role of water in exciton recombination processes. We have also made significant advances in Raman spectroscopy of carbon nanotubes, enabled by recent availability of samples highly enriched in a single structure. Raman characterization has also been used to improve such separation processes. Important discoveries include the demonstrating strong asymmetry in the resonance Raman excitation profiles of semiconducting nanotubes and our recent extension of the generality of this behavior to include metallics and to probe this response for varying transitions and phonon modes.

Two-dimensional electronic systems, such as graphene, possess many unique optoelectronic properties such as the tuneability and dispersion of 2D plasmons that may afford mesoscopic device integration. Through CINT user programs we are studying graphene plasmons using resonant energy transfer approaches and purely optical techniques - such as broadband infrared interferometry. We show, for example, that by monitoring the fluorescence quenching from a semiconductor nanoparticle-graphene system the complete dispersion and a lifetime of graphene plasmons can be obtained.



NPON Postdoc YoungShin Park

# First Infrared Quantum Dots to Stop Blinking

*Scientific Achievement*

Non-blinking excitonic emission from near-infrared (NIR) and type-II nanocrystal quantum dots (NQDs) is reported for the first time, coupled with suppressed Auger recombination (AR). To realize this unusual degree of stability at the single-dot level, novel InP/CdS core/shell NQDs were synthesized for a range of shell thicknesses (~1–11 monolayers of CdS).

*Significance*

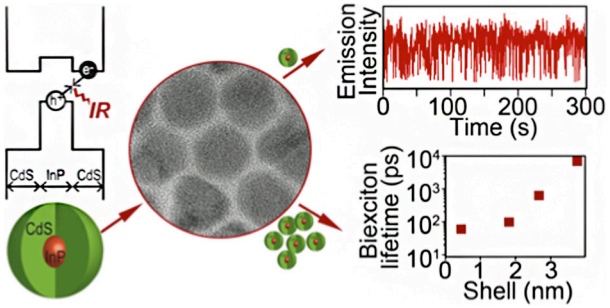
This new system demonstrates that electronic structure and shell thickness can be employed together to effect control over key single-dot and ensemble NQD photophysical properties. Suppressed-blinking, NIR emitting NQDs are ideal candidates molecular probes for single-particle tracking; suppressed AR has important implications for optical amplification and lasing.

*Research Details*

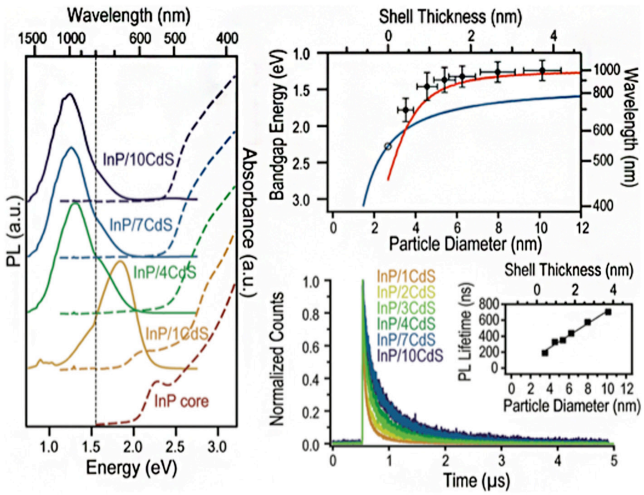
- Ensemble spectroscopy measurements (photoluminescence peak position and radiative lifetimes) and electronic structure calculations established the transition from type-I to type-II band alignment.
- Single-NQD studies revealed clear evidence for blinking suppression that was not strongly shell-thickness dependent, while photobleaching and biexciton lifetimes trended explicitly with extent of shelling.
- Specifically, very long biexciton lifetimes–up to >7 ns–were obtained for the thickest-shell structures, indicating dramatic suppression of AR.

*Reference*

A.M. Dennis, B.D. Mangum, A. Piryatinski, Y.-S. Park, D.C. Hannah, J.L. Casson, D.J. Williams, R.D. Schaller, H. Htoon, J.A. Hollingsworth, Nano Lett. 12, 5545 (2012).




Type-II InP/CdS core/shell NQDs afford non-blinking emission at the single-dot level and suppressed Auger recombination.




Ensemble spectroscopy data reveal rapid transition to a type-II charge-transfer emission state upon CdS shelling of the InP cores. Left: significantly red-shifted emission and absorption progressively dominated by CdS shell (<520 nm) with increasing shell thickness. Top right: core/shell bandgap (red) defies that for core-only InP of equivalent size (blue). Bottom right: Significantly increasing emission lifetimes as a function of shell thickness.

# Dielectric Resonator Metamaterials at Optical Frequencies

*Scientific Achievement*

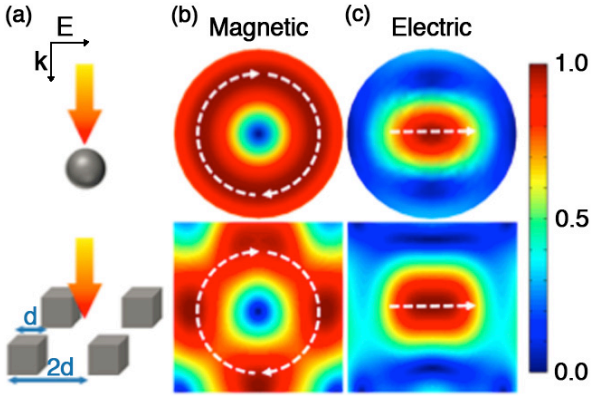
We demonstrate, for the first time, an all-dielectric metamaterial composite in the midinfrared based on micron-sized, high-index tellurium dielectric resonators

*Significance*

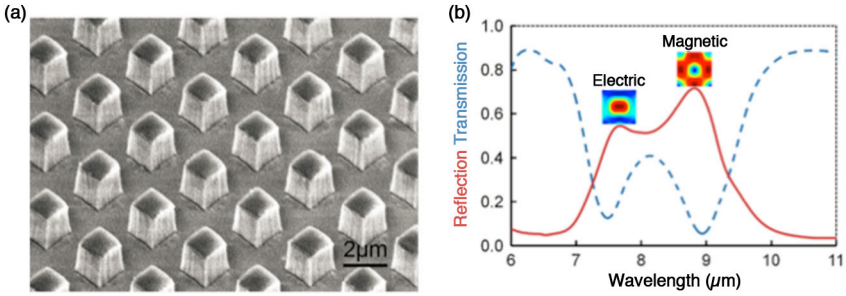
Dielectric resonators are desirable compared to conventional metallodielectric metamaterials at optical frequencies as they are largely angular invariant, free of Ohmic loss, and easily integrated into three-dimensional volumes. This work represents a first step toward the development of passive low-loss, isotropic artificial magnetic conductors, magnetic mirrors, hard or soft surfaces, and subwavelength cavities in the infrared.

*Research Details*

- A 1.7mm thick film of Te was deposited on the surface of a BaF2 optical flat via electron-beam evaporation, patterned using electron-beam lithography, and etched using a reactive ion etching process.
- the patterned wafer was characterized using a hemispherical directional reflectometer). Both the simulation and the experiment clearly show two resonances with corresponding peaks in the reflection coefficient and minima in the transmission coefficient. The magnetic resonance in the simulated coefficients is at 8.9mm and shows good agreement with the experimentally observed feature at 9mm.




(a) Excitation configuration of an isolated sphere (top row) and an infinite two-dimensional cube array with 1:1 duty cycle (bottom row). Normalized electric field distribution is shown for the (b) first- and (c) second-order modes in the sphere and cubic resonators. White dashed lines and arrows indicate field direction..




(a) Scanning electron micrograph of a fabricated CDR array. (b) Measured reflection (solid [red] curve) and transmission (dashed [blue] curve) coefficients for the CDR array. Field patterns from Fig. 1 are shown above each corresponding resonance.

*Reference*

J.C. Ginn, I. Brener, D.W. Peters, J.R. Wendt, J.O. Stevens, P.F. Hines, L.I. Basilio, L.K. Warne, J.F. Ihlefeld, P.G. Clem, and M.B. Sinclair, PRL 108, 097402 (2012)

# Nanoscale Electronics and Mechanics Thrust

**Quanxi Jia, Thrust Leader; Brian Swartzentruber, Partner Science Leader**

This thrust is focused on understanding and controlling electrical and mechanical properties arising from confinement on the nanoscale, interactions within nanostructures, and the integration of heterogeneous nanostructures for much improved and/or novel functionalities. Reduced dimensions as well as the influence of surfaces and interfaces can give rise to emergent functionalities not found in micro- and macro-scale systems. For electronic and mechanical systems, important integration issues involve energy transfer across interfaces, the role of defects in nanostructured materials, and interactions between nanoscale building blocks in integrated structures. These scientific issues arise in both electrical and mechanical nanosystems as we bring nanostructures together to implement specific functions, combine different materials to manipulate electrical or mechanical behaviors, and/or control the defect landscapes in given nanostructured materials for desired structural and functional properties.

**Recent Accomplishments:** Our accomplishments in 2012 are reflected in a wide range of topical areas including nanowires and nanowire heterostructures, high-mobility 2D based III-V materials and 1D quantum devices, nanomanipulation and integration of nanostructures, mechanical responses in nanostructured metals, novel nanobatattery assembly and testing platforms, effects of surface/interface on the functionalities of complex materials, and discovery platforms.

**Single Spin Devices**: Semiconductor nanoelectronic devices exhibit novel quantum mechanical properties individually, and integration of multiple quantum systems provides a strong approach to making single spin devices. In our thrust, we are working on techniques to create devices where we control and measure the spin of single electrons in silicon. Fabrication techniques are uniquely suited to make very advanced silicon devices, and in addition, the predominance of $^{28}Si$ (92% in natural silicon) with zero nuclear spin leads to extremely long energy and coherence lifetimes. We are working on creating various approaches to work with single electrons in silicon and developing high speed all-electrical measurements of single electron spins. These include double quantum dots, time-resolved spin readout of a single electron in a semiconductor, and as part of an active user project spintronics using high mobility GaAs 2DEGs.

**Nanoscale Plasticity and Fracture**: In recent years, the ability to image localized plasticity events during small-scale mechanical testing has become critical to understanding nanomechanical behavior. In situ mechanical measurements in the SEM provide an ideal combination of sufficient spatial and temporal resolution of these events, but require specialized mechanical test stages to deform the material under the appropriate imaging conditions. CINT installed a Hysitron PI-85 SEM Picoindenter in August 2012. This system provides the capability to deform materials via nanoindentation, tension, compression, or bending. This equipment excels in testing small samples or volumes with critical dimension <1 μm. For larger samples, or for the high loads encountered when testing nanocomposites, when intrinsic rather than extrinsic (e.g. layer thickness vs. sample size) effects are to be measured, the load capacity of commercially available in situ deformation stages is inadequate. At CINT, we have designed and built a custom nanomechanical deformation stage to address these needs. A user project on determining bond strength and fracture behavior of Al-Zr-U/10Mo nuclear fuel elements uses this capability. Due to the ~1 mm thickness of the fuel element, conventional large-scale testing is unfeasible, making nanomechanical testing an ideal method for investigating mechanical behavior.

**Nanocomposite Metal-oxides**: Non-toxic, thick, ferroelectric films with a high Curie temperature (TC) are required for numerous applications. Many replacement systems for $PbZr_xTi_{1-x}O_3$ are being studied, a prominent example being bismuth layered compounds. While Tc for these materials can be high, up to 790 °C, property optimization is difficult due to the need for careful textural alignment. $BiFeO_3$ and other titanate perovskites are alternative high TC ferroelectrics; however processing windows are narrow and doping needs to be extremely precise. Through joint effort with CINT users (both Prof. MacManus-Driscoll from University of Cambridge and Prof. Wang from Texas A&M University), we have successfully synthesized self-assembled nanoscale composites of $BaTiO_3$ (BTO) and $Sm_2O_3$ (SmO) up to 1.25 mm thick that exhibit tetragonality up to at least 800 °C and strong remnant polarization to at least 330 °C (potential for ferroelectricity up to 800 °C. The enhanced Tc is a consequence of uniform, vertical strain coupling between stiff 10 nm regular interspersed nanocolumns of SmO and a surrounding BTO nanomatrix, preventing the onset of the tetragonal to cubic phase transition. The nanocomposite structure improved BTO crystalline quality and reduced the leakage current. The much enhanced Curie temperature in thick-film BTO has opened a new approach to use BTO in high-temperature ferroelectric applications. We, in collaboration with CINT users (both Prof. MacManus-Driscoll and Prof. Wang), have also created a nanoscaffold nanocomposite ferroelectric material containing $Ba_{0.6}Sr_{0.4}TiO_3$ (BSTO) and SmO. Strained vertical nanopillar heteroepitaxial films of $(Ba_{0.6}Sr_{0.4}TiO_3)_{1-x}$:$(Sm_2O_3)$ x show remarkably improved tunability values at the same time as reduced dielectric loss. This behavior is opposite to what has been demonstrated in any previous report. This new kind of nanostructure and composition holds great promise for electrically tunable microwave devices operating at room temperature and above. The vertical strain controlling mechanism represents a new paradigm to design tunable microwave dielectrics.

**Nanowire Growth and Characterization:** We resolved conflicting issues of size effects on vapor-liquid-solid (VLS) nanowire growth through a comprehensive study. Our research clearly revealed Gibbs Thomson effects in nanowire growth by measuring the growth rate with different catalyst sizes and precisely controlled vapor pressure. By the virtue of the nature of the VLS growth process in semiconductor nanowires and their small size, the nucleation, propagation, and termination of stacking defects in nanowires are dramatically different from that in thin films. We demonstrated Ge-Si axial nanowire heterostructure growth by the VLS method with 100% composition modulation and used these structures as a platform to understand

how defects in stacking sequence force the ledge nucleation site to be moved along or pinned at a single point on the triple-phase circumference, which in turn determines the nanowire morphology. Combining structural analysis and atomistic simulation of the nucleation and propagation of stacking defects, we explained these observations based on preferred nucleation sites during nanowire growth. This study provided basic foundations for an atomic level understanding of crystalline and defective ledge nucleation and propagation during [111] oriented NW growth and improves understanding for control of fault nucleation and kinking in nanowires. Synthesis of Ge-Si core-shell nanowire heterostructures is typically accompanied by unwanted gold diffusion on the Ge nanowire sidewalls, resulting in rough surface morphology, undesired whisker growth, and detrimental performance of electronic devices such as the source–drain leakage current and the transconductance of a field effect transistor. We advanced understanding of this Au diffusion on nanowires, its diameter dependence and its kinetic origin. We devised a growth procedure to form a blocking layer of Si grown between the Au seed and Ge nanowire sidewalls that leads to elimination the Au diffusion for in situ synthesis of high quality Ge-Si core-shell heterostructures. For advanced device applications, increasing the compositional abruptness of axial heterostructured and modulation doped nanowires is critical for optimizing performance. For nanowires grown from metal catalysts, the transition region width is dictated by the solute solubility within the catalyst. When the solute solubility in the catalyst is lowered, the heterojunction width can be made sharper. We showed for the first time the systematic increase in interface sharpness between axial Ge-Si heterojunction nanowires grown by the VLS growth method using a AuGa alloy catalyst. Through in situ tailoring of the catalyst composition using trimethylgallium, the Ge-Si heterojunction width is systematically controlled by tuning the semiconductor solubility within a metal AuGa alloy catalyst. Spatially-resolved composition analysis reveals that the interfacial width of AuGa-catalyzed Ge-Si axially-heterostructured nanowires is decreased by a factor of 2 over Au-catalyzed ones. We demonstrate the shortest transistor channel length (17 nm) fabricated on a VLS grown silicon nanowire by a controlled reaction with Ni leads on an in situ TEM heating stage at a moderate temperature of 400°C. $NiSi_2$ is the leading phase, and the silicide–silicon interface is an atomically sharp type-A interface. At such channel lengths, high maximum on-currents of 890 (μA/μm) and a maximum transconductance of 430 (μS/μm) were obtained, which pushes forward the performance of bottom-up Si nanowire Schottky barrier field-effect transistors (SB-FETs). Our device results corroborate with our transport simulations and reveal a characteristic type of short channel effects in SB-FETs, both in on- and off-state, which is different from that in conventional MOSFETs, and that limits transport parameter extraction from SB-FETs using conventional field-effect transconductance measurements.

**Magellan HRSEM_**

An FEI Magellan 400 Scanning Electron Microscope was installed at the CINT Gateway, and has been available to users since Fall 2012. This state-of-the-art electron microscope provides sub-nanometer spatial resolution from 1 kV to 30 kV. By using low voltages, only the surface of the sample interacts with the electron beam and thus insulators and beam-sensitive samples can be imaged without the need for conductive coatings maximizing the amount of surface data. These capabilities make this tool ideal for investigations of nanotubes, nanowires, nanocomposites, and other materials where workhorse SEMs do not have the low-voltage resolution required for sensitive surface imaging. This new microscope specifically features:

- Schottky thermal emission source with UniColore mode to give a highly coherent beam (less than 0.2 eV energy spread)
- Spatial resolutions of 0.8 nm at 1 kV and above in secondary electron mode
- EDAX Apollo XV Energy Dispersive Spectroscopy (EDS) detector for elemental analysis
- EDAX Hikari Electron Backscatter Diffraction (EBSD) detector for crystallographic orientation determination
- Electron beam lithography patterning capability, and
- Annular STEM detector (spatial resolution of 0.7 nm)

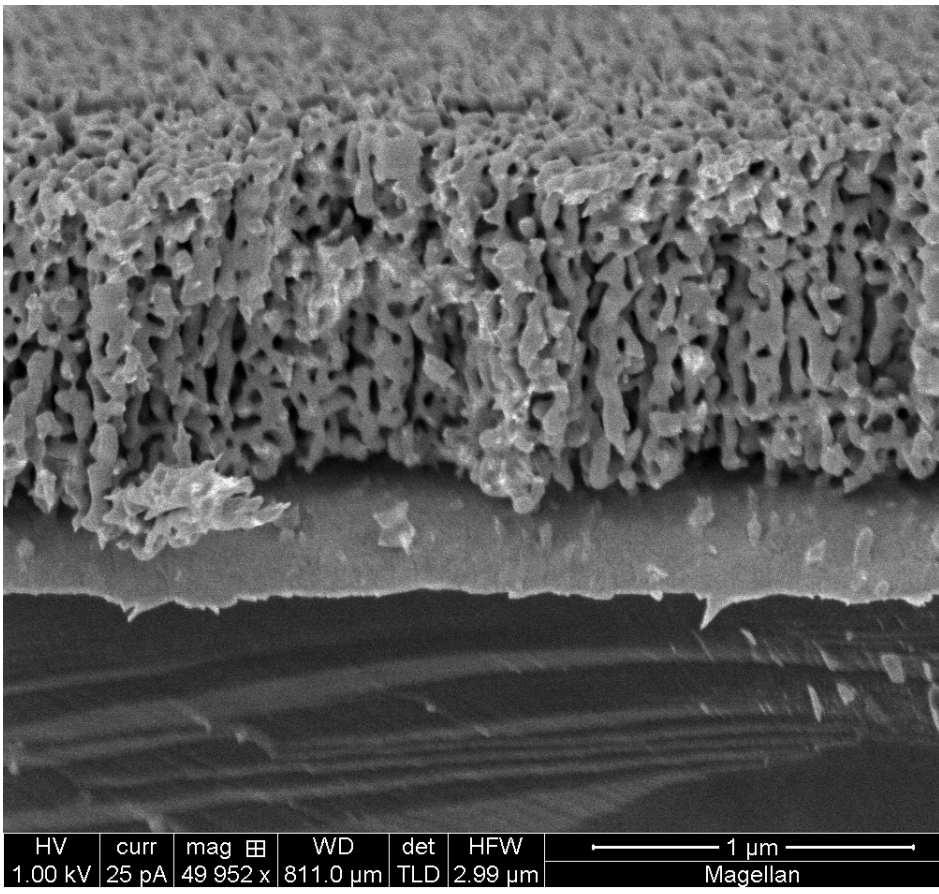



Figure 15: Image of Gold nanofoam taken with the Magellan HRSEM.

# Cellular complexity captured in durable silica biocomposites

*Scientific Achievement*

We fabricated cell/silica composites (CSCs) and converted them to silica replicas using mammalian cells as scaffolds to direct complex structure formation. Inter- and intra-cellular heterogeneity from the nano- to micro-scale is captured and dimensionality is preserved following drying and exposure to extreme temperature, which allows for size and shape preserving pyrolysis of cellular architectures to form conductive carbon replicas.

*Significance*

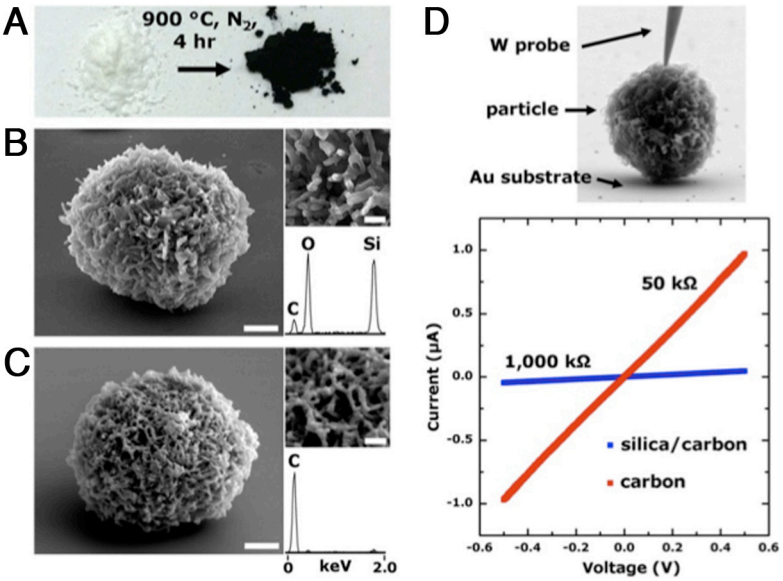
Translation of cellular architectures into inorganic materials provides routes to generate hierarchical nanomaterials with stabilized structures and functions. The structural and behavioral malleability of the starting material (cultured cells) provide opportunities to develop robust and economical biocomposites with programmed structures and functions.

*Research Details*

- We used the nanomanipulator at CINT to measure the electrical conductivity of CSC particles after pyrolysis, pre- and post silica etching (Fig. D) and find a 20-fold decrease in their electrical resistance.

*Reference*

B. Kaehr, J. L. Townson, R. M. Kalinich, Y. H. Awad, B. S. Swartzentruber, D. R. Dunphy, and C. J. Brinker, PNAS 109, 17336 (2012).




Shape-preserving carbonization of 4T1 CSCs. (A) Pyrolysis of CSCs produces an opaque powder comprised of particles that have retained cellular structure (C). Etching of the silica produces a carbon rich replica. (D) In situ electrical characterization of carbonized particles shows a 20-fold decrease in electrical resistance across a particle following silica etching. (Scale bars, B and C: 2 μm; Insets, 500 nm).

# Extremely High Tunability and Low Loss in Nanoscaffold Ferroelectric Films

*Scientific Achievement*

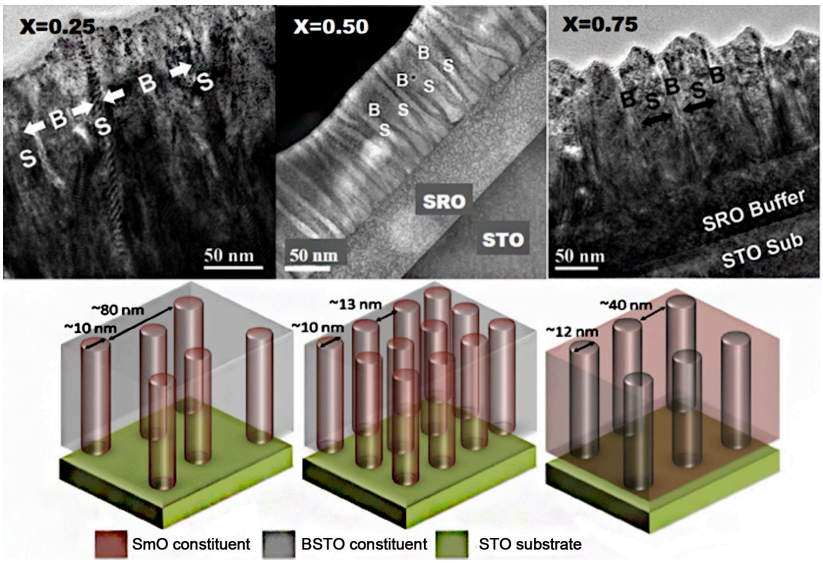
We have created a nanoscaffold nanocomposite ferroelectric material containing $Ba_{0.6}Sr_{0.4}TiO_3$ (BSTO) and $Sm_2O_3$. Strained vertical nanopillar heteroepitaxial films of $(Ba_{0.6}Sr_{0.4}TiO_3)_{1-x}(Sm_2O_3)_x$ show remarkably improved tunability values at the same time a reduced dielectric loss. This behavior is opposite to what has been demonstrated in any previous report.

*Significance*

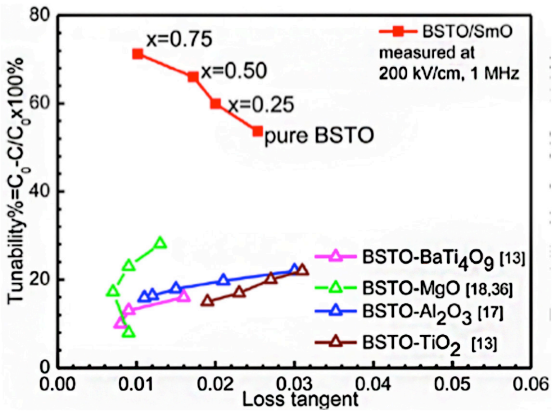
This new kind of nanostructure and composition holds great promise for electrically tunable microwave devices operating at room temperature and above. The vertical strain controlling mechanism represents a new paradigm to design tunable microwave dielectrics.

*Research Details*

- CINT's well controlled pulsed laser deposition system enabled the growth of desired vertically strained nanocomposites with desired structural and physical properties.
- Tunability values of 75% (200 kV/cm field) were achieved at room temperature in micrometer thick films, the value remaining to >50% at 160 °C. Low dielectric loss values of <0.01 were also achieved, significantly lower than reference pure BST films.




TEM cross sections of the films $(Ba_{0.6}Sr_{0.4}TiO_3)_{1-x}(Sm_2O_3)_x$ for x = 0.25, 0.5, and 0.75 together with the schematics of corresponding pillar-like nanostructures.




Tunability vs. loss tangent for 600 nm films with $Sm_2O_3$ fraction, x, as a parameter on the plot. Also shown on the plot are composite films from the literature. The trend for our nanocomposite films directly contrasts to other standard composite films.

*Reference*

L. O. Lee, S. A. Harrington, A. Kursumovic, E. Defay, H. Wang, Z. Bi, C.-F. Tsai, L. Yan, Q. X. Jia, and J. L. MacManus-Driscoll, Nano Lett. 12, 4311 (2012).

# Soft, Biological & Composite Nanomaterials Thrust

**Steve Doorn, Acting Thrust Leader; George Bachand, Partner Science Leader**

The Soft, Biological and Composite Nanomaterials Thrust focuses on solution-based nanomaterials, and targets improved understanding of how to integrate disparate classes of materials to produce functional results. Inspiration is drawn from a long-term grand challenge in nanoscale materials research, which is to be able to mimic the exquisite structures and functions that Nature produces through the synthesis, assembly, reconfiguration and exploitation of disparate components. Activities of the Thrust are directed toward key scientific areas:

1. Controlling interfaces and interactions between disparate classes of materials across multiple length scales;
2. Developing and applying new characterization tools for studying soft, biological and composite systems on multiple length and time scales; and
3. Exploring the roles of disorder and dynamics in controlling the performance of functional soft, biological and composite materials.

Within this framework, topics include synthesis of multi-component nanoscale building blocks, assembly of components using both active and passive assembly methods, development of instrumentation for characterization of complex, disordered and dynamic composite materials, the study of dynamic and reconfigurable surfaces and interfaces, the incorporation of soft or biological materials into microscale device architectures, and the development of membrane-based composite materials.

Recent Accomplishments:

**Interactions of Nanomaterials with Biological Materials:**
*Nanoparticle* – cell interactions. Work integrating both CINT science and external collaborators Jeri Timlin and Jessie Aaron (SNL) has used a variety of microscopy techniques (e.g., total internal reflectance fluorescence and hyperspectral confocal microscopy) to evaluate how NP morphology controls their interactions with biomembranes and cells. Studies performed on natural cell membranes determined that the NP aspect ratio strongly regulates the interaction. Rod-shaped particles were found to diffuse slower (~10 fold) and internalize at a significantly slower rate (2-3 fold) than spherical particles. Hyperspectral confocal microscopy further evaluated the region of NP localization within biomembranes. In other studies conducted in collaboration with Susan Brozik (SNL) and Jean Clare Seagrave (Lovelace Respiratory Research Institute, NM), the interaction of Au and Ag NPs with primary human lung cells showed that the smaller particles (i.e., 20 vs. 60 nm), regardless of composition ligand type or metal, induces significant inflammatory response (i.e., secretion of cytokine, IL-8) despite the absence of cytotoxicity. Lastly, a user project with Rashi Iyer (LANL) evaluated the effect of size, surface charge, and functionalization on primary human lung cells. Here, the interactions were shown to be dependent on collective chemical and physical properties that could be roughly ranked, from greatest to least impact, as nanoparticle surface charge, ligand length, and size.

*Synthesis of nanomaterials for transformative biodetection and imaging.* Noble metal nanoclusters (NCs) exhibit fluorescence emission spanning the UV to NIR and are gaining significant interest due to their tunable photophysical properties and biomediated synthesis. In the area of detection, a DNA probe (NanoCluster Beacon, NCB) that "lights up" upon target binding has been developed. The NCB has a signal-to-background noise of up to 500 and has proven to be a powerful probe for DNA detection. "Chameleon" NCBs that can change their fluorescence emission based on the identity of the single nucleotide polymorphism in the vicinity of the NC have been produced. The binding specificity of DNA-templated AgNCs will ultimately prove useful as a fluorescent reporter for the imaging of mRNA trafficking in live cells. Full implementation of NCs for application in bioimaging, however, requires further improvements in their fluorescence and environmental stability and biocompatibility. Toward this end, recent efforts have succeeded in evolving DNA sequences that template NCs exhibiting increased pH and temperature stability (pH 4.9; $T_m$ = 75 °C).

Technologist Mietta Lillo prepares samples for a user project.

*Spatio-temporal imaging on the nanoscale.* The unique CINT 3-D tracking microscopy capability was applied by B. Wilson (UNM) and Diane Lidke (UNM) to study the 3D spatiotemporal dynamics of Q dot labeled individual proteins responsible for the human allergic response. The work measured single protein – protein interactions and dynamics throughout the 3D volume of a living cell. The down-regulation and dynamics of the receptor being endocytosed was captured and the internal transport kinetics of the process was determined to be ca. 950 nm /s. In other studies, the 3D diffusive motion of individual Green Fluorescent Protein (GFP) and organic dyes were also successfully tracked at μm2 / s.

*A molecular view of cellulose activity.* The use of enzymes to aid in the dissolution of the carbohydrate polymer (cellulose) and aromatic polymer (lignin) offers a means to greatly reduce the cost of biofuel production from an abundant feedstock. The enzyme-catalyzed hydrolysis of cellulose is a complex process that is not well understood. Single-molecule imaging techniques developed by Goodwin and co-workers have been used to directly elucidate the molecular-level details of cellulase activity on cellulose. Total internal reflection fluorescence microscopy (TIRFM) has been used to monitor the movement of individual fluorescently-labeled cellulases interacting with insoluble cellulose substrates. Time-resolved, super-resolution single-molecule fluorescence imaging has recorded the motion of multiple individual cellulases with nm spatial resolution. The collected images showed that under hydrolysis conditions (pH 5), the majority (> 90%) of the cellobiohydrolase (TrCel7A) molecules were stationary to within the ~15 nm resolution of our measurement, while ~5% of the population translated with rapid, linear, sliding motion.

**Functional Nanostructured Materials:**

*Reconfigurable artificial biomembranes.* Montano and co-workers examined the pH-responsive behavior of a single component lipid bilayer. Specifically, membrane deformations such as lipid caps, budding vesicles, and large invaginated structures reminiscent of cellular organelles were all imaged by AFM and fluorescence microscopy. Similar lipid membrane deformations have been observed previously by other groups, but this work represents the first demonstration of such deformations occurring in a single component system. These studies suggest a novel path for using environmental shifts as a means to alter lipid packing. The membrane proteins instability is believe to arise from an insufficient water layer.

*Transport in artificial biomembrane.* Paxton and co-workers have examined the transport of H+ and OH- across poly[ethylene oxide-b-butadiene], EOnBDm, vesicle membranes. Polymersomes and liposomes were prepared via gentle rehydration. The permeability, P, was determined by monitoring the fluorescence of a pH-sensitive fluorophore (hydroxypyrenetrisulfonate) contained within the polymersomes. These studies showed that the permeability was reduced by a factor of 3 compared to standard lipid vesicles. The increased permeability was attributed to the membrane thickness compared to typical lipid bilayers. However, we determined that ion permeability across polymer vesicles was highly dependent on the chemical composition of the polymer. Thus, the ion transport in polymersomes offers greater tunablity than lipid-based systems. In addition, we have confirmed that polymer vesicles with non-hydrolysable end groups are capable of sustaining substantially higher concentration gradients in more extreme pH environments (pH > 10 or pH < 4) relative to liposomes.

*Phase separation in diblock copolymers.* Progress in the area of directing diblock phase separation into well-ordered, device compatible structures has been limited due to several noted drawbacks of diblock copolymers, including the need to spin coat onto planar substrates followed by slow annealing protocols to induce ordering. Huber and co-workers have examined both experimentally and computationally (with Theory thrust scientists and users) phase-separation in mixed homopolymer monolayers. Collectively, these studies showed that when compositionally different polymers are anchored to a common surface, phase separation occurs that is conceptually similar to the familiar behavior of diblock copolymers. Recent work has focused on developing a molecular-level understanding of the phase separation of poly(methyl methacrylate)-b-polystyrene, PMMA-PS. Self-consistent field theory (SCFT) was used to predict a phase diagram of the PMMA-PS system. Experimental determination of the phase behavior was conducted and revealed significant differences in the details of the predicted structures.

*Biomembrane-inorganic materials integration*. Nanoporous (NP) Au and Pt thin films have been prepared using a two-step etching process developed by Dattelbaum and co-workers. The nanoporous metal films produced using this method have minimal cracking and pitting. A mixture of lipids, including a thiol-terminated lipid, 1,2-Dipalmitoyl-sn-Glycero-3-Phosphothioethanol (DPPTE; 59.5 mol%), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC; 39.5 mol %), and 1-oleoyl-2-6-[(7-nitro-2-1,3-benzoxadiazol-4-yl)amino] hexanoyl-sn-glycero-3-phosphoethanolamine (NBDPE; 1 mol%), was used to prepare vesicles that were deposited via vesicle fusion on a NP- Au surface. The DPPTE lipids bind to the gold surface to stabilize the lipid assemblies, yet fluidity is retained at room temperature. Fluorescence images from a Fluorescence Recovery after Photobleaching (FRAP) experiment of the POPC/DPPTE lipid membrane on a NP-Au substrate reveal that the resulting lipid membranes are fluid with a diffusion constant of 0.26 μm2/s. In general, mobile lipids in native biological membranes and lipid membranes on solid supports move with a diffusion constant of ~0.5-10 μm2/s. Electrochemical impedance spectroscopy (EIS) indicated that formation of DPPTE:POPC lipid assemblies on NP-Au resulted in at least two orders of magnitude increase in impedance, as well as a significant increase in capacitance. To our knowledge, this is the first example of a lipid membrane supported on nanoporous metal supports with demonstrated fluidity and resistivity, which are critical features for mimicking natural biological membrane function.

# Effects of potential environmental interferents on kinesin-powered molecular shuttles

*Scientific Achievement*

Biomolecular active transport represents Nature's means for solving issue concerning the materials transport at the nanoscale. By reconstructing biomolecular active transport ex vivo, the robust nature of kinesin biomolecular motor-transport of microtubule filaments was demonstrated against a wide range of potential environmental interferents.

*Significance*

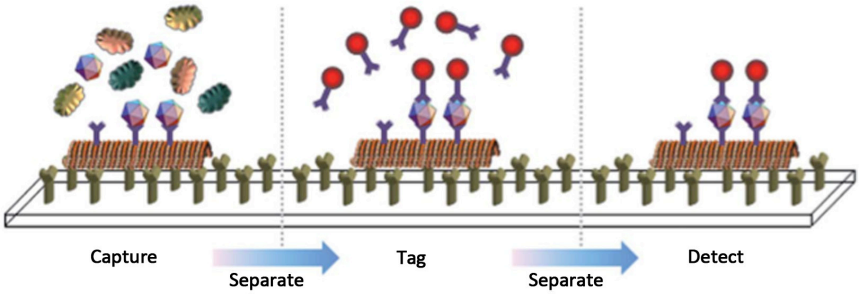
Fully retained and even improved kinesin-drive transport of microtubule shuttles in the presence of contaminating solvents and environmental compounds possibly detrimental to emerging, ex vivo applications. Future implementation of kinesin motors as nanofluidic transporters will enable remote sensing of biological analytes without the need for electrical energy.

*Research Details*

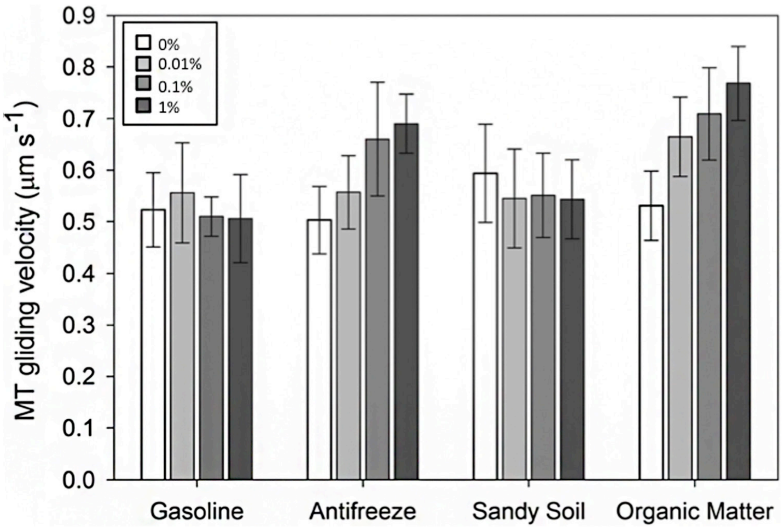
- Kinesin-microtubule active transport was reconstructed ex vivo, and characterized following the addition of various potential environmental contaminants.
- Fluorescence microscopy shows that transport is maintained and may be enhanced dependent on the added compound.

*Reference*

Marlene Bachand and George D. Bachand, Nanoscale 4, 3706 (2012).




Schematic diagram of a kinesin-motor driven system for capture and detection of bioanalytes for remote detection




Kinesin-driven molecular shuttles show no significant decrease in velocity due to potential interferents/contaminants. Rather, velocities increased when antifreeze or organic matter was added.

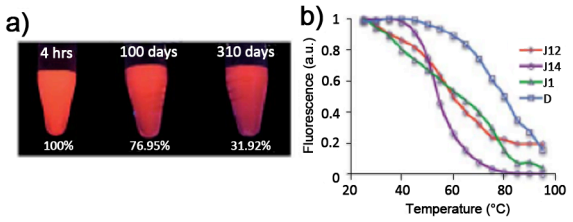
# Evolving fluorescent DNA-templated silver nanoclusters

*Scientific Achievement*

Through systematic evolution of DNA, we have produced DNA sequences that template highly stable fluorescent silver nanoclusters (AgNCs). In contrast to other DNA templated silver nanoclusters that have a relatively short shelf-life, the fluorescent species templated in this new DNA sequence retains significant fluorescence for at least a year. Moreover, this new silver nanocluster possesses low cellular toxicity and enhanced thermal, oxidative, and chemical stability.

*Significance*

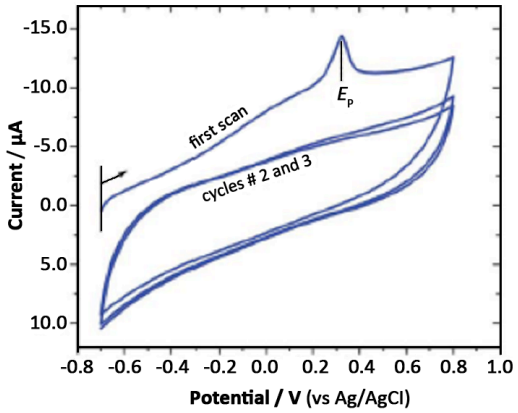
AgNC are new optical moieties (~1 nm size; 2-31 atoms), templated directly within DNA. To utilize the clusters as biological labels or for building nano and mesoscale assemblies we seek clusters that are universally fluorescent and transferable for integration. Most DNA-templated silver nanoclusters can neither be integrated with other materials nor are they resistant to oxidation, and subsequent loss of fluorescence. We have shown that DNA can be systematically evolved to produce clusters with enhanced optical activity. This work lays the ground work to develop high-throughput methods of cluster evolution and selection of clusters tailored toward specific applications.




Evolved clusters are stable for nearly a year (a). Altered secondary structure of the DNA (as determined by CD) provides a more stable template environment, yielding a cluster with increased stability to oxidation, temperature (b) and the biological milieu.

*Research Details*

- New AgNC are stable for 310 days (versus 2 weeks for unevolved DNA). Newly evolved DNA has secondary structure atypical of other DNA sequences that template AgNC, suggesting that the secondary structure is a stabilizing element.
- New clusters are far more stable in the reduced state than are other clusters and silver nanoparticles.




Cyclic voltammogram of D-AgNC. Increased fluorescence, stability and temperature resistance correlates to increased resistance to silver oxidation.

*Reference*

J. Sharma, R.C. Rocha, M.L. Phipps, H.-C. Yeh, K.A. Balatsky, D.M. Vu, A.P. Shreve, J.H. Werner, J.S. Martinez "A DNA-templated fluorescent silver nanocluster with enhanced stability" Nanoscale 4, 4107 (2012).

# Theory & Simulation of Nanoscale Phenomena Thrust

**Gary Grest, Thrust Leader; Jianxin Zhu, Partner Science Leader**

The Theory and Simulation of Nanoscale Phenomena Thrust focuses on identifying the fundamental concepts that control the unique behavior of integrated materials and systems with nanoscale structure. As the relative strengths of various interactions change with length scale, competition between interactions can lead to spontaneous self-organization at characteristic length scales. In integrated nanosystems, these intrinsic length scales can couple to naturally occurring or artificially imposed nanoscale inhomogeneity leading to the coexistence of different types of ordering and/or emergent phenomena.

The various components of an integrated nanosystem each have their own intrinsic properties. This provides freedom to control and optimize system behavior. Conversely, successful nanoscale integration requires control over the interactions between components, which must be weak enough to maintain the unique properties of the nanoscale components, but strong enough that the components interact in order to achieve new properties and functionality. Improved understanding of how the interactions in nanosystems can be controlled through integration and how novel behavior emerges as a result of integration will help optimize particular functionality and even achieve multifunctional and/or responsive materials and systems. Therefore, this thrust aims to understand the role of novel and competing interactions in nanoscale integration. This effort is organized into three science directions that together form the basis for integration at the nanoscale:

1. Nanoparticles in Complex Environments,
2. Excitation and Transport in Nanostructured Systems, and
3. Nanodomain/Nanostructure Interactions.

**Recent Accomplishments:**

*Nanoparticles at Complex Interfaces*. Coarse-grained molecular dynamics simulations have been used to calculate the diffusion D constant for cylindrical transmembrane proteins in a lipid bilayer as a function of radius R. Recent theoretical calculations have found that D scales as 1/R, when hydrodynamic interactions are important. This result contrasts with the standard Saffmann-Delbrück expression that has a logarithmic scaling. Recent experimental simulations have found both dependencies in an apparent contradiction. Our simulation data can be equally well fit by both theories, and we find that the different dependencies of D for typical values of R can be indistinguishable. In collaboration with CINT Users X.-M. Lin and H. Jaeger, Grest is using MD simulations to study alkanethiol coated gold NPs at the water/vapor interface. Jaeger and Lin have shown that two-dimensional NP membranes have unusually high GPa moduli with remarkable potential as ultrathin filtration devices. As one of the key outstanding issues concerns the origin of the membranes' ability to sustain large tensile stress, we are currently investigating the mechanical strength of the dry NP membranes after the water is removed. Other work in this area includea following the aggregation of highly anisotropic 2 nm diameter alkanethiol NPs at the water/vapor interface and the behavior of gold NPs grafted with amine terminated linear hydrocarbon chains in water.

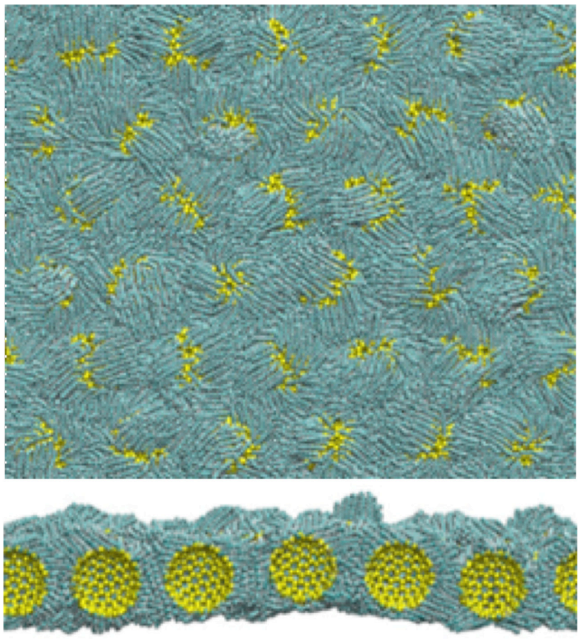


Figure 16: Snapshot of dry membrane consisting of 36 4 nm diameter alkanethiol coated gold NPs with $S(CH_2)_{17}CH_3$ ligands. Top and side views.

*Structure on the Nanoscale.* M. Stevens and A. Frischknecht with CINT user K. Winey have studied the ionic aggregate morphology in a series of linear poly(ethylene-co-acrylic acid) (PEAA) ionomers with precise spacing between acid groups neutralized with Li+ using fully atomistic MD simulations in order to treat varying neutralization levels and to determine the atomic details of the ionic and hydrogen bonding interactions. We unexpectedly found that ionic aggregate morphology, including string-like and percolated aggregates, varies strongly as a function of the neutralization level. In addition, aggregate formation relies on hydrogen bonds as well as ionic association. Stevens (CINT) performed MD simulations of the single-molecule experiments of ssDNA performed by CINT user O. Saleh. Over the range of salt concentrations and valences, the simulation results quantitatively match the recent experimental data. The

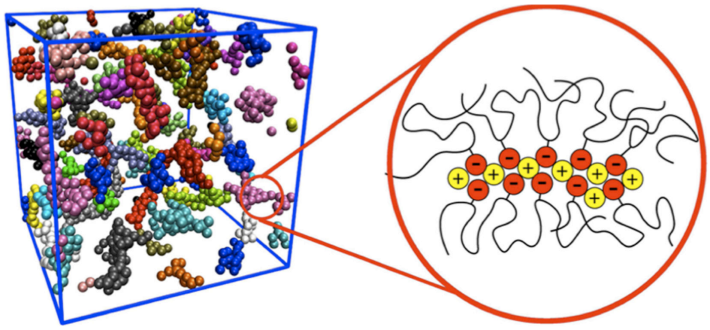


Figure 17: Visual representations of ionic aggregates. Representative snapshot from 43% neutralization system, where coloring is by aggregate. Only aggregates with two or more counterions are shown. Image on right shows schematic of stringy aggregate morphology.

simulations determined the origin of the mysterious logarithmic elasticity seen in experiments to be the wrinkled, short range structure of the flexible ssDNA. Grest and Users M. Robbins and D. Perahia used MD simulations to study how the strength of welded and self-healing interfaces grows as the degree of interdiffusion across the interface increases. Our simulations show that the interfacial strength saturates at the bulk shear strength long before polymers diffuse by their radius of gyration. Along with the strength increase, the dominant failure mode changes from chain pullout at the interface to chain scission as in the bulk.

**Excitation and Transport in Nanostructured Systems**

*Energy Harvesting, non-adiabatic excitation and quasiparticle dynamics.* TSNP Scientist S. Tretiak in collaboration with CINT User V. Chernyak continued to extend ideas from the Exciton Scattering theory to establish a universal quasiparticle framework allowing treatment of complex electronic dynamics (e.g., exciton dissociation/recombination into charges, electron/spin dynamics, and phonon induced processes) in integrated nanosystems. Recently, we have further extended these ideas to incorporate electron-phonon coupling into a computationally tractable model of the nanometer length-scale and sub-nanosecond timescale dynamics of excited electron-vibrational states, which are essential to determining molecular electronic properties. To simulate non-adiabatic excited state molecular dynamics, Dr. Tretiak in collaboration with CINT Users S. Fernandez-Alberti (Buenos Aires) and A. Roitberg (University of Florida) used surface hopping techniques combined with excited state potential energy surfaces obtained from semi-empirical and ab initio techniques accounting for many-body effects. Subsequently, we have developed novel Non-Adiabatic Excited State Molecular Dynamics (NA-ESMD) framework for modeling excited state dynamics and radiationless relaxation in large molecular systems., state crossing occur constantly during the dynamics of the system, and the appropriate techniques are still a matter of research. Furthermore, in such systems, it becomes useful to talk about an electronic temperature, which may or may not be in equilibrium with the ionic temperature in a particular nanosystem. The electrons exchange energy with the ions and contribute to electronic heat conduction and thermoelectric behavior. Systems where the thermal properties of electrons are important include thermoelectric generators and refrigerators, where electrical energy is obtained directly from temperature differences or vice versa, radiation resistant materials, where nanoscale thermal transport controls the initial annealing of radiation damage cascades, and modern electronic devices, where the ability to remove heat from nanoscale features is becoming a fundamental limitation on device performance. There is considerable interest from the CINT user community in modeling larger, bulk-like nanostructures having essentially a continuous density of states. To date, our efforts have focused on using Ehrenfest dynamics within the Time-Dependent Density Functional Theory (TDDFT) to simulate the exchange of energy between electrons and ions in these systems. A careful analysis of the results demonstrates that Ehrenfest dynamics does a good job of capturing the transfer of heat from ions to electrons, but fails to properly account for the transfer of heat from electrons to ions due to the absence of quantum correlations between the electrons and ions in the Ehrenfest method. As part of this work, we have developed a method for directly creating a thermalized electronic state within the TDDFT.

*Understanding Tunneling Experiments.* We have calculated the electronic local density of states (LDOS) of DNA nucleotide bases (A,C,G,T) deposited on both graphene and graphene with SiC substrate. Our calculations have revealed significant base-dependent HOMO-LUMO features in the LDOS that serve as electronic fingerprints for individual bases. We have also obtained the angular dependence of the LDOS peak position. We have also simulated the single-base DNA electronic structure on graphene with a SiC substrate, and observed that the orbitals of the DNA bases are spread over the SiC despite the separating layer of graphene. Transport through molecular junctions has many of the same features and theoretical challenges as STM experiments. CINT Scientist Zhu has recently developed semi-exact quantum many-body theory within the nonequilibrium Green's function approach to investigate the thermoelectric transport in a single molecular junction with both electron-phonon coupling and electron-electron interactions. We have generalized this approach to study the electrical and thermal transport through a quantum wire

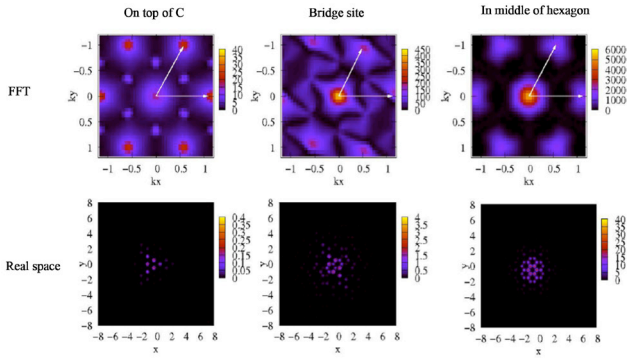



Figure 18: Real Space and FT QPI images of Kondo resonance depending on atomic position of atom on graphene.

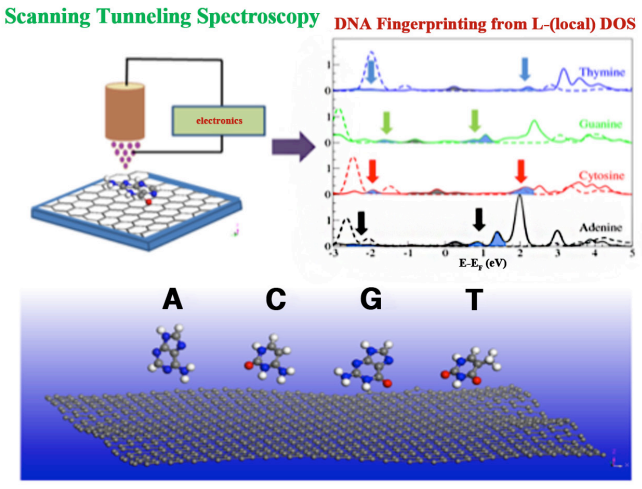



Figure 19: Schematic diagram of STM, local DOS and single molecular DNA bases on Graphene.

with both electronic correlation and coupling to vibrational modes. We have investigated with user Wehling, the site and hybridization dependence of the Kondo effect of ad atoms on graphene. We have calculated spectroscopic features and quasiparticle interference effects for all these adsorbtion sites. In the two-impurity Anderson model, the inter-impurity spin-exchange interaction favors a spin-singlet state between two impurities, leading to the breakdown of the Kondo effect. CINT Scientist Zhu together with his collaborator has showed that a local uniform magnetic field can delocalize the quasiparticles to restore the Kondo resonance. Within the same two-impurity Anderson model, Zhu has been able to define a composite fermion and study its coherent excitations. Motivated by the recent success of local electron tunneling into heavy-fermion materials, CINT Scientists Zhu and Balatsky and co-workers have studied the local electronic structure around a single Kondo hole in an Anderson lattice model and the Fano interference pattern relevant to STM experiments.

**Emergent Behavior at Surfaces and Interfaces**

*Emergent Properties*. In collaboration with CINT users and NPON and NEM CINT scientists, we have designed and interpreted experiments using ultrafast optical probes of nanosystems. We have measured and modeled the ultrafast dynamics of coupled ferromagnetic, antiferromagnetic, and ferroelectric order in multiferroic $TbMnO_3$ films. We also conducted and modeled a terahertz spectroscopic study of the magnetoelectric excitations in $BiFeO_3$, and ultrafast carrier dynamics in the presence of coexisting ferroelectric and antiferromagnetic order. Using a phenomenological approach, we have examined the modified electronic states at the interface between ferro(para)electric and superconducting or magnetic heterostructure. We have found that electric polarization P order parameters can be significantly modified due to coupling through linear terms brought about by explicit symmetry breaking at the interface. Using an effective action and a Ginzburg-Landau formalism, we have showed that an interaction term that is linear with respect to the electric polarization ($\lambda P_{zl} |\psi_{zl}|^2$ or $\lambda P_{zl} M_{zl}^2$) will induce a polarization in the paraelectric state through the coupling to the superconducting order parameter $\psi$ or magnetization (M) at the interface. We have also showed that a FE polarization will produce a modulation of the SC or M order parameter.

*Surface and Interface Structure.* Working with CINT Users at the University of Michigan, we have developed a powerful approach combining Kohn-Sham density functional theory, rule-based enumeration, the cluster expansion method, and Monte Carlo simulations to systematically explore possible surface structures while accounting for the effects of temperature and compositional variation. These techniques have been applied to help explain experiments investigating the nanoscale structure of GaAs, InGaAs, GaSb, and GaAsBi bulk and heterostructure surfaces. We have also began to apply our approach to systematically identify the structure of interfaces with initial efforts focused on the $ZnO/Cu_2O$ interface, which is technologically interesting due to possible applications as an earth abundant solar cell material.

# Femtosecond Torsional Relaxation

*Scientific Achievement*

Using ultrafast spectroscopy and theoretical excited state dynamics simulations, we demonstrate optical control over the molecular shape in the case of oligofluorene by photoexciting a specific state, introducing concepts of 'quantum kick' and 'quantum brake' in the conformational space.

*Significance*

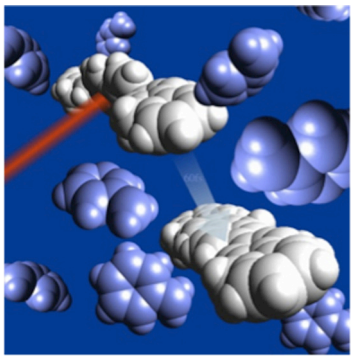
Conjugated polyfluorenes are technologically important materials being blue emitters in organic LEDs (OLEDs) devices. Our joint theoretical/experimental studies changed our understanding on how fast a single photon can alter the molecular shape, and have important implications for OLED technology.

*Research Details*

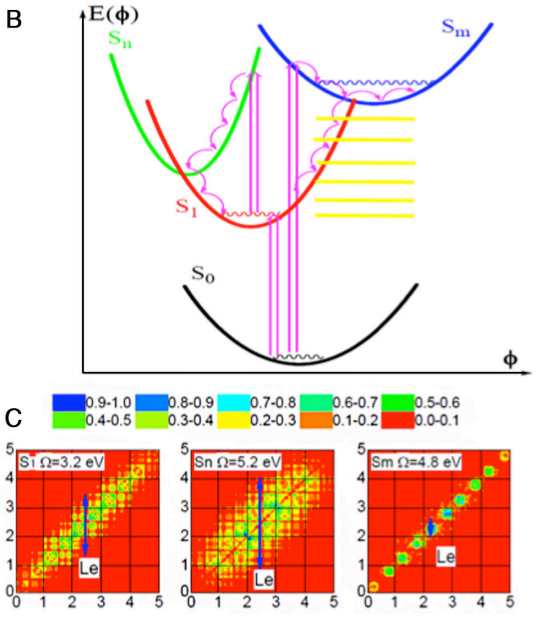
- State-of-the-arts pump-probe transient absorption spectroscopy with a computer-controlled delay line with ~5 fs accuracy has been used to probe relaxation dynamics of several selected molecular states.
- Recently LANL-developed non-adiabatic excited-state molecular dynamics (NA-ESMD) code was used to model non-adiabatic excited-state dynamics in a photoexcited polyfluorenes and rationalize experimentally observed relaxation timescales and concomitant conformational motions.

*Reference*

J. Clark, T. Nelson, S. Tretiak, G. Cirmi, and G. Lanzani, Nature Physics, 8 225 - 231 (2012).



Ultrafast spectroscopy of polyfluorenes reveals fascinating ultrafast (~100fs) relaxation of the highly excited state Sn back to the first excited state S1, being one of the fastest conformational processes known in nature).




Our concurrent theoretical modeling confirmed experimental data and explained mechanisms leading to such excited-state-specific ultrafast relaxation

# Optical Properties of Nanorod/Polymer Assemblies

*Scientific Achievement*

Optical absorption due to surface plasmon resonances in gold nanorod/polymer composites strongly depends on nanorod separation and orientation.

*Significance*

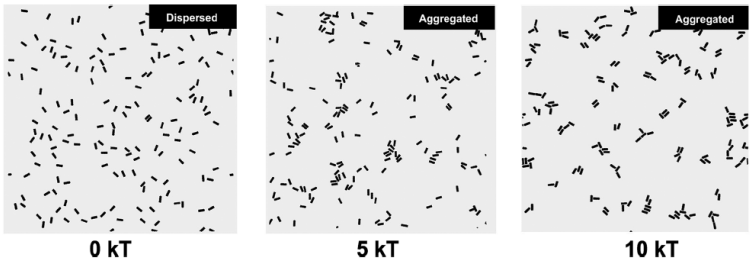
Metal nanorod/polymer composite films with tunable optical properties can be predictably engineered and conveniently manufactured.

*Research Details*

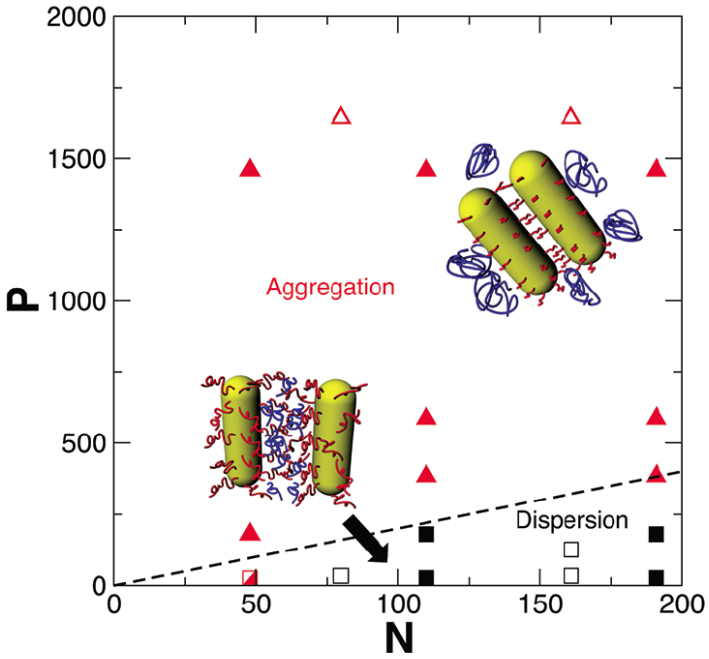
- Gold nanorods in polystyrene thin films are dispersed for brush chain lengths that exceed the polystyrene matrix chain length and are aggregated otherwise.
- UV/vis experiments and discrete dipole approximations together demonstrate the correlation of nanorod morphology and optical absorption response.
- Monte Carlo simulations using parameters from density functional theory calculations elucidate the underlying interactions responsible for the observed behavior.

*Reference*

Michael J. A. Hore, Amalie Frischknecht and Russell Composto, *ACS Macro Letters*, (2012) 1, 115




Monte Carlo configurations of nanorods as a function of increasing depletion–attraction energy (ε). As the inter-rod attraction increases, the morphology changes from dispersed to partially aggregated and finally to strongly aggregated.




Dispersion map of PS-Au(N):PS(P) films showing how the degree of polymerization of the matrix and brush, N and P, determine nanorod morphology. Squares correspond to composites with isolated NRs that are dispersed in PS, and triangles correspond to NRs that form aggregates in PS. In addition to PS-Au(N):PS(P) (solid symbols), the morphology for the PEG-Au(N):PEO(P) system is also given (open symbols). The dashed line corresponds to P = 2N and represents the transition between aggregation and dispersion. The morphology of PS-Au(48):PS(26) is ambiguous and represented by the half-shaded symbol.

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## Distinguished Affiliate Scientists

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Antoinette Taylor (Los Alamos)

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# Awards granted in 2012

**CINT STAFF**

A. Dattelbaum, Winner of Postdoctoral Distinguished Mentor Award at LANL

S. Doorn, Winner of the LANL Fellows Prize for Research

A, Frischknecht, Fellow of the American Physical Society

A. Frishknecht, Appointed to Editorial Advisory Board for Macromolecules and ACS Mictoletters

Q. Jia, Selected as American Association for the Advancement of Science Fellow

N. Li, Winner of Postdoctoral Distinguished Performance Award at LANL

N. Mara, Winner of the TMS Young Leaders Professional Development Award

J. Martinez, Kavli Fellow

J. Martinez, Winner of Postdoctoral Distinguished Mentor Award at LANL

A. Misra, Selected as a Los Alamos National Laboratory Fellow

W. Paxton, Early Career Research and Development Award, SNL

T. Picraux, Winner of Postdoctoral Distinguished Mentor Award at LANL,

M. Stevens, Sandia Outstanding Mentor Award

**USERS**

J. Bird, Recipient of SUNY Chancellor's Award for Excellence in Scholarship & Creative Activities

J. Bonca, 2012 Zois Award - highest Slovene award given for science. There is only one given per year for all natural sciences in Slovenia

J. Carpenter, Los Alamos National Laboratory Postdoctoral Distinguished Performance Award: Honorable Mention

J. Carpenter, The Minerals, Metals & Materials Society Young Leader Professional Development Award

P. Clem, Elected to IEEE Ultrasonics, Ferroelectrics and Frequency Control Society (IEEE UFFC-S) governing Administrative Committee

E. Flynn, CINT related research selected as exemplar project by the National Cancer Institute of the National Institutes of Health.

D. Gianola, DOE Early Career Award

R. Goldman, Fellow of the American Vacuum Society

R. Goldman, Fellow of the American Physical Society

M. Hagman, Appointed as a Research Professor in Electrical and Computer Engineering at the University of Utah

Q. Hu, Recipient of the IEEE Photonics Society William Streifer Scientific Achievement Award

A. Kocharian, Elected Foreign Member of Armenian National Academy of Sciences

S. Kumar, Lehigh University. P.C. Rossin Assistant Professorship at Lehigh University

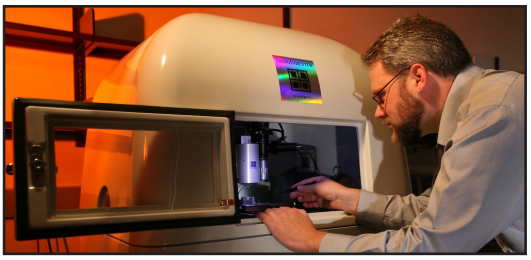
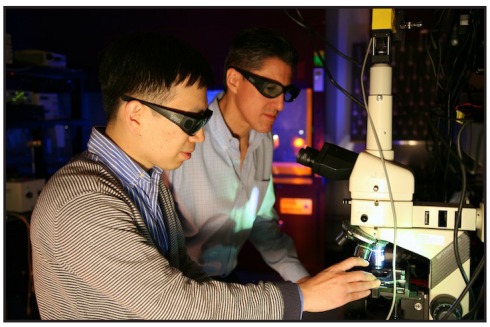
H. Luo, Recipient of 2012 Early Career Award from NMSU University Research Council for Exceptional Achievements in Creative Scholarly Activity

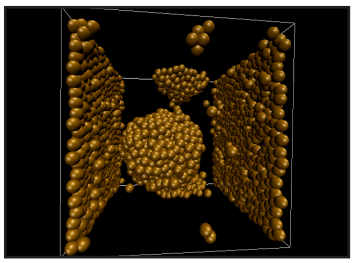
N. Chawla, Editor – Materials Science and Engineering A

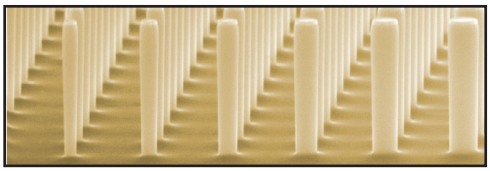
N. Chawla, Fulton Professor of Materials Science and Engineering – Arizona State University

J. Shelnutt, The cover of two issues of the Journal of Porphyrins and Phthalocyanines dedicated for user's 65th birthday.

J. Zide, Department of Energy Career Award






Center for Integrated Nanotechnologies
DISCOVERY PERFORMANCE EDUCATION INTEGRATION
CINT
Sandia Los Alamos

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